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Identification and Analysis of Polychlorinated Biphenyls and other Related Chemicals in Municipal Sewage Sludge Samples

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IDENTIFICATION AND ANALYSIS OF POLYCHLORINATED BIPHENYLS AND OTHER RELATED CHEMICALS IN MUNICIPAL SEWAGE SLUDGE SAMPLES

AUGUST 1977

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
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ABSTRACT

Methods were developed for the extraction, clean-up and GC/MS analysis of polychlorinated biphenyls (PCBs) and related chemicals in municipal sludge samples. Each of the sludge samples received from nine major United States cities was processed to yield a neutral fraction and two acid fractions which were methylated with dimethylsulfate and diazomethane, respectively. Samples were cleaned up by silica gel column chromatography. A total of 35 chlorinated compounds were found in the full scan GC/MS analysis, including polychlorobiphenyls, polychloronaphthalenes, polychloroaniline, polychlorobenzene and DDE. Some chlorinated compounds remain unidentified.

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LIST OF ABBREVIATIONS

ACD - Diazomethane-methylated fraction of sewage sludge.
DDE - 1,1-Dichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)-ethylene or 1,1-Dichloro-2,2-bis(p-chlorophenyl)-ethylene.
GC - Gas chromatography.
GC/MS - Gas chromatography/mass spectrometry/computer.
HX - Hexane eluate from silica gel column chromatography.
m/e - Mass-to-charge ratio.
MID - Multiple ion detection.
MTH - Dimethylsulfate-methylated fraction of sewage sludge.
MW - Molecular weight.
NE - Neutral extract fraction of sewage sludge.
PCB - Polychlorinated biphenyl.
RMR - Relative Molar Response.
RSD - Relative Standard Deviation.
SD - Standard Deviation.
TIC - Total Ion Current.
TL - Toluene eluate from silica gel column chromatography.

1.0 INTRODUCTION

Polychlorinated biphenyls (PCBs) are stable, highly persistent chemical compounds used primarily as dielectrics in electrical systems and as plasticizers. Because of their wide-spread use, they are found in all parts of the environment. Due to their capability to bioaccumulate, they present a serious human health hazard.(1) The environmental dangers presented by PCBs have been deemed to be so great that their manufacture will be discontinued after January, 1979 in the United States (Toxic Substances Control Act, 1976). Their use, properties, environmental effects, and levels have been reviewed.(1)

Analysis of sludge is indicative of the environmental pollution caused by the release of this substance. The sludge may eventually be digested far enough to be reinjected into the sewage plant effluent, it may be dried and transported to landfills, or it may be used as agricultural fertilizer and soil builder. If PCBs or other halogenated organics are present, they may eventually enter the human food chain. PCBs with low chlorine equivalents have been shown to photodegrade to dimers and dibenzofuran analogs(2) and to metabolize to various phenolics, anisoles, and benzoic acids.(2) Thus, presence of these compounds in sludge is also of interest.

2.0 SUMMARY AND CONCLUSIONS

Methods were developed for the extraction, cleanup and GC/MS analysis of municipal sludge samples. The samples were analyzed and the data interpreted.

Sludge samples from wastewater treatment plants in nine United States cities were collected by Regional EPA personnel and Research Triangle Institute (RTI).

Each of the nine sewage sludge samples was prepared to yield a neutral fraction and two acid fractions which were methylated with dimethylsulfate and diazomethane, respectively. A portion of each sample was retained as is, but the majority was chromatographed on silica gel to yield two fractions, the hexane eluate and the toluene eluate. Thus, each of the nine samples was fractionated into 3 x 3 = 9 fractions for a total of 81 samples for analysis. Since analysis of all 81 sample fractions would have been unwieldy and redundant, only the most promising fractions were analyzed. The workup procedures as executed for this task are listed in Appendix A. The sample fractions were analyzed using a quadrupole gas chromatograph/mass spectrometer/computer (GC/MS/COMP) using a non-polar (OV-101) column. All methods used were validated with spiked samples.

A total of 35 chlorinated compounds were found, including polychlorobiphenyls, polychloronaphthalenes, polychloroanilines, polychlorobenzenes and DDE. Most chlorinated compounds remain unidentified. No brominated compounds were observed.

A fraction of the sludge obtained in New Bedford, Massachusetts contained a total PCB concentration of 10,800 μg/ℓ with the trichloro- and tetrachlorobiphenyl isomers predominating.

The detection of phenolics in the neutral extract and of unmethylated phenolics in the acid fractions indicates that the sample preparation procedures are not totally satisfactory. The methylation reactions may not be quantitative because of an excess of acid equivalents in the sample extracts.

3.0 RECOMMENDATIONS

Six major areas of research need to be expanded and pursued to improve the methods used here:

(1) The methylation reactions must be investigated more closely. It appears that the conditions used were insufficient to methylate some compounds of interest.

(2) The entire sample preparation procedure, including the column chromatography, may be improved to eliminate more interferents and enhance the detection of trace components.

(3) Complementary analytical methods should be used to verify the GC/MS identification. One such method would be gas chromatography/Fourier transform infrared (GC/FTIR) spectroscopy.

(4) Quantitation of the compounds of interest should be pursued.

(5) An exhaustive study, taking into account the more volatile components and involving more cities must be pursued.

(6) Future studies should concentrate on correlating the occurrence of chlorinated compounds with the type of sample. This would include water treatment procedures, sewage treatment procedures, and possible industrial sources.

4.0 OBJECTIVES

The major emphasis on this research was to analyze municipal sludge samples for PCBs and related compounds by GC/MS. The specific objectives were to (1) develop methods of extraction, derivatization, and cleanup which yield samples containing PCBs and related compounds amenable to analysis; (2) establish GC/MS conditions to analyze the sample fractions; (3) analyze the sample fractions; and (4) interpret the data and identify halogenated compounds.

5.0 METHOD DEVELOPMENT

The methods used in this task were primarily adapted and refined from literature methods. The most applicable methodology found was that developed by Keith.(3-9) The primary objective of this research was specifically directed toward the extraction of neutral compounds for the detection of PCBs. Two methylation procedures were invesigated for derivatization of phenolics and carboxylic acids.

5.1 CHEMICALS AND INSTRUMENTATION

All solvents used were distilled in glass (Burdick and Jackson, Muskegon, MI) and used without further purification. Where purity was especially critical, solvents were redistilled in glass. Aroclor® mixtures, and pesticides were obtained from the Quality Assurance Section, Environmental Toxicology Division, EPA, HERL, Research Triangle Park, NC; individual PCB isomers and chlorobiphenyls were obtained from RFR Corp., Hope, RI; 2-chloro-5-methoxyphenol was obtained from Aldrich Chemical Co., Milwaukee, WI; anthracene was obtained from Matheson, Coleman, and Bell, East Rutherford, NJ, and silica gel was obtained from Davison Chemical Division, W. R. Grace, Maryland, MD.

Analysis of all samples for PCBS and related compounds was accomplished using a Finnigan 3300 quadrupole GC/MS with a PDP/12 computer as discussed in Section 5.3.1.

5.2 DEVELOPMENT OF SAMPLE EXTRACTION AND WORKUP PROCEDURES

5.2.1 Extraction of Neutral and Basic Compounds

The extraction of neutral and basic components in sludge was accomplished at pH 11 using chloroform. Details of the procedure are listed in Appendix A.

The method was validated for PCBs by analysis of spiked samples. Samples of water and sludge from the Raleigh, North Carolina municipal treatment facility were spiked with ∿100 μg each of mono-, di-, tri-, tetra-, penta-, hexa- and decachlorobiphenyl and a 1N NaOH solution added until the pH was approximately 11. The samples were extracted four times with chloroform (~50 ml portions) for 10-15 min each using a mechanical reciprocal shaker at ~60 cpm. The combined extracts were dried on Na_2SO_4 and the solvent evaporated first in a Kuderna-Danish apparatus and then under a nitrogen stream.

Gas chromatography/mass spectrometry (GC/MS) analysis of the sample indicated that all PCB isomers were being extracted (Figure 1, Table 1) with an overall recovery of 70% for monochlorobiphenyl and >90% for all other PCBs tested.

5.2.2 Methylation of Acidic Components with Dimethylsulfate

After extraction of the neutral components, the acidic components of the sludge fraction were methylated using dimethylsulfate and extracted with chloroform.(3) The details of the procedure are listed in Appendix A.

The method was evaluated using Raleigh sludge spiked with about 300-400 μg each of 3,3',5,5'-tetrachloro-4,4'-biphenyldiol, 3-chloro-4-biphenylol, pentachlorophenol (PCP), 2,3,6-trichlorophenylacetic acid (Fenac), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2-chloro-5-methoxyphenol. The methylated derivatives of the two biphenyls and of PCP were observed in the GC/MS analysis (Figures 2 and 3).

The effect of pH on the extraction of the methylated compounds from the aqueous sample was investigated with the spiked solutions. The methylated product was divided into two equal portions which were extracted in parallel at pH = 11 and 7.5 to control all other variables. A comparison of the integrated peak areas for the parent ions of the three compounds is presented in Table 2. These results indicated extraction at pH = 11 is more than twice as efficient as that at pH = 7.5 Based on these results, the methylated phenolics were extracted at pH = 11.

Thus, it appeared that the dimethylsulfate methylation works well for phenolic compounds, but not for carboxylic acids. Therefore, a methylation reaction using diazomethane was used to methylate the carboxylic acid fraction.

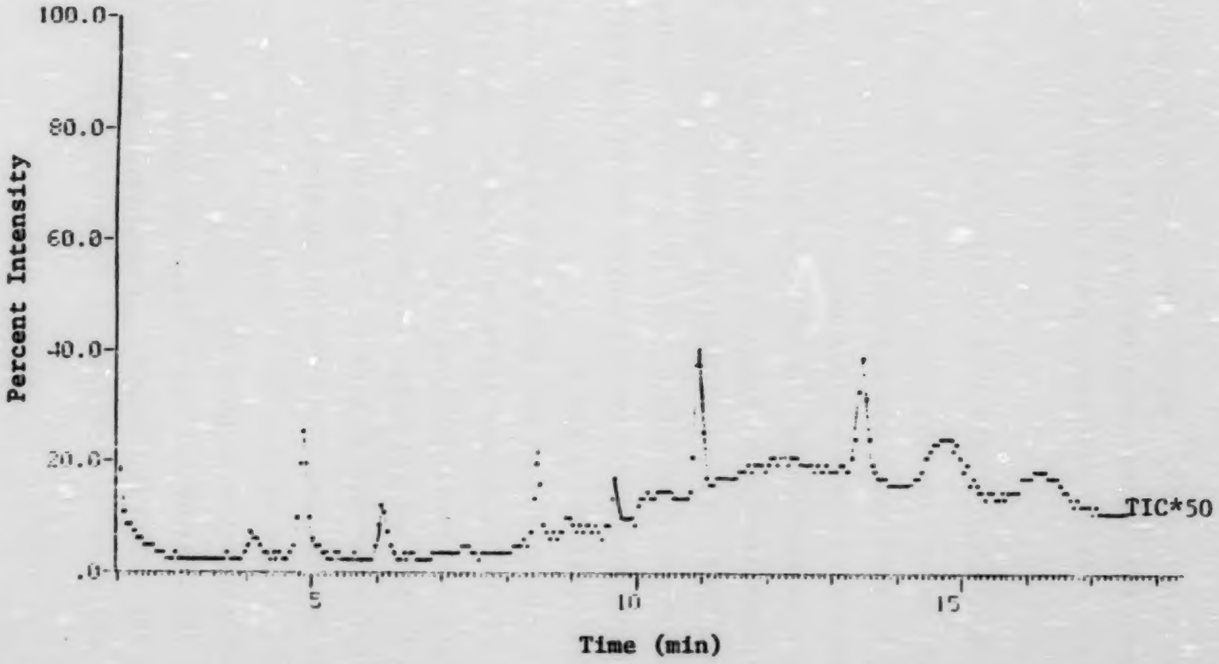


Figure 1. GC/MS TIC chromatogram of neutral extract of Raleigh sewage sludge spiked with PCBs.

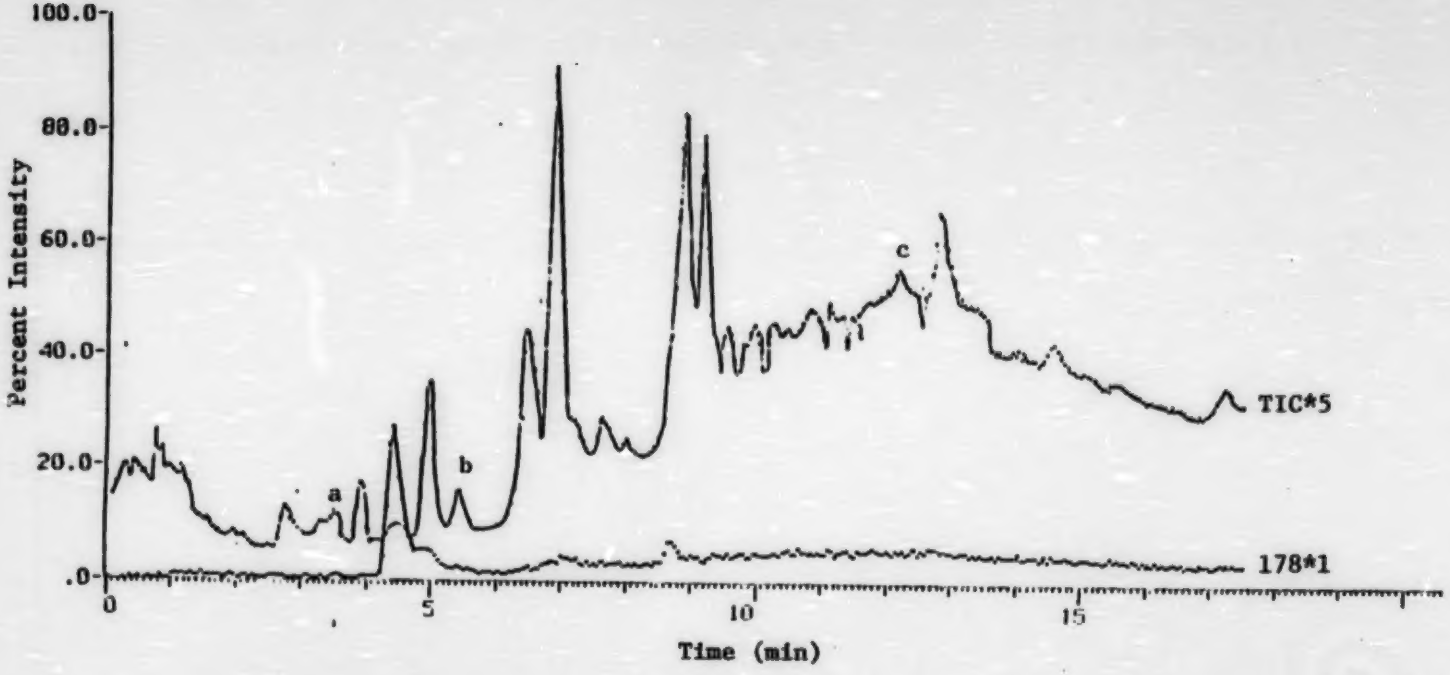


Figure 2. GC/MS analysis of spiked sludge - methylated phenolics extracted at pH = 11.
a - pentachloroanisole
b - 3-chloro-4-methoxybiphenyl
c - 3,3',5,5'-tetrachloro-4,4'-dimethoxybiphenyl

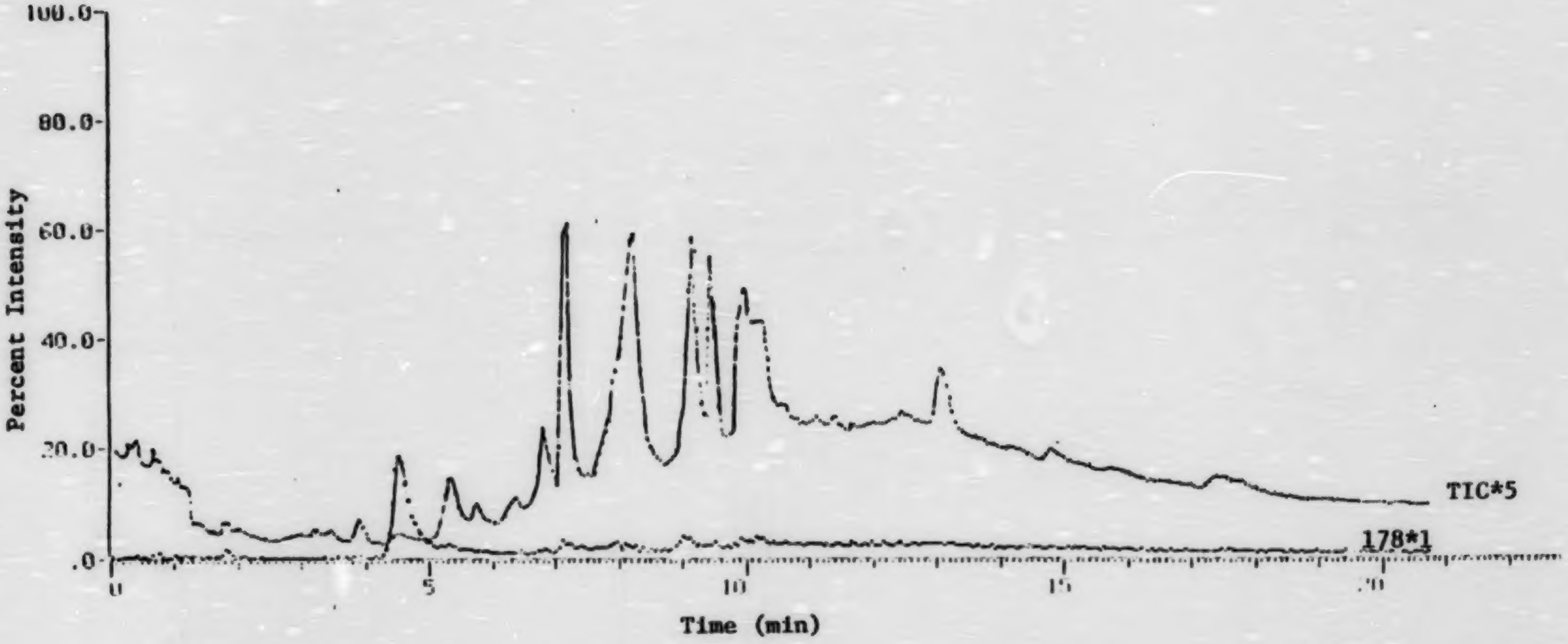


Figure 3. GC/MS analysis of spiked sludge-methylated phenolics extracted at pH = 7.5.

Table 1. PCBS RECOVERED FROM NEUTRAL EXTRACT OF SPIKED RALEIGH SLUDGE

Compound	Retention Time (min)[a]
$C_{12}H_9Cl_1$	1.9
$C_{12}H_8Cl_2$	4.8
$C_{12}H_7Cl_3$	6.0
$C_{12}H_6Cl_4$	8.4
$C_{12}H_5Cl_5$	9.6
$C_{12}H_4Cl_6$	10.9
$C_{12}Cl_{10}$	18.3

[a] Chromatographic column conditions were 150° for 3 min, then 8°/min to 230° and then held at the upper limit.

Table 2. EXTRACTION EFFICIENCY OF METHYLATED PHENOLICS AT TWO pH VALUES

Compound	Relative Response[a]	
	pH = 7.5[b]	pH = 11
pentachloroanisole	0.049	0.128
3-chloro-4-methoxy-biphenyl	0.194	0.386
3,3',5,5'-tetrachloro-4,4'-dimethoxybiphenyl	0.063	0.139

[a] Arbitrary response value obtained by ratio of integrated areas of parent ions of anthracene standard and sample compound.

[b] Extraction pH. See text for experimental details.

5.2.3 Methylation of Acidic Components with Diazomethane

Using a separate aliquot of sludge, the acidic components of the sludge were extracted with chloroform at pH = 2 and then methylated using diazomethane. The details of the procedure are listed in Appendix A.

The method was evaluated in the same manner as the dimethylsulfate methylation (Section 5.2.2). The TIC chromatogram of this sample is shown in Figure 4 and the compounds found in Table 3. The 2-chloro-5-methoxyphenol was only partially methylated and the 3-chloro-4-biphenylol was not recovered. The other compounds were methylated, however.

5.2.4 Column Chromatography

Since initial GC/MS results indicated that the background was interfering with detection of PCBs and related compounds, a column chromatographic step was instituted. A portion (0.25) of each sample was retained as is, but the majority (0.75 ml) was chromatographed on silica gel to yield two fractions, the hexane eluate and the toluene eluate. The procedure was previously tested and validated in these laboratories.(6) PCBs and other halogenated organics were found to elute in the hexane fraction, while most chlorinated pesticides (heptachlor, DDT, lindane and others) and polar organics were eluted by toluene. The details of the procedure are listed in Appendix A.

5.2.5 Summary

The flow diagram in Figure 5 summarizes the extraction and workup steps for sludge samples. For each sludge sample, a total of nine fractions were generated.

5.3 DEVELOPMENT OF INSTRUMENTAL METHODS

5.3.1 GC/MS Analysis of PCBs

Analysis of all samples for PCBs was accomplished using a Finnigan 3300 quadrupole GC/MS with a PDP/12 computer. The 180 cm x 2 mm i.d. glass column, packed with 2% OV-101 on Chromosorb W was held at a temperature of 120° for three min, programmed to 230° at 12°/min and held isothermally until all peaks had eluted. Helium flow was 30 cc/min. The ionization voltage was nominally 70 eV and detector voltages were between 1.8 and 2.2 kV. Full scan spectra were obtained from m/e 110-500. Analysis for method development and some initial samples were conducted under the temperature

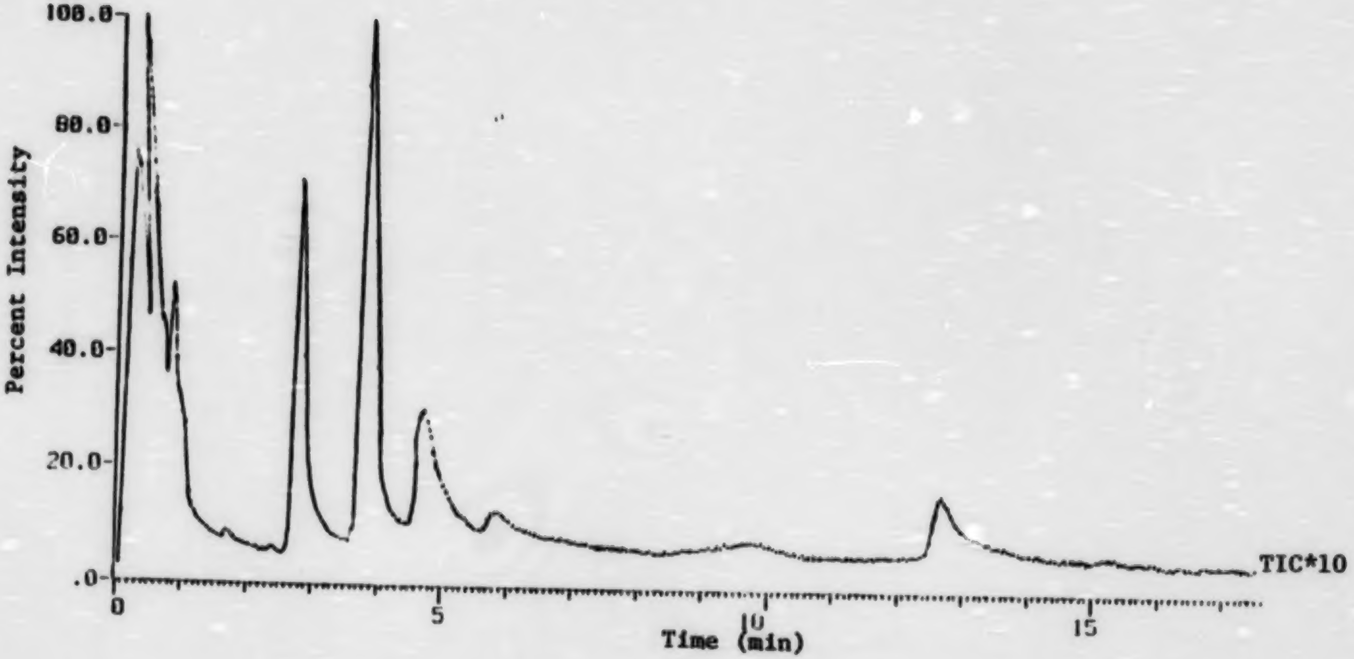


Figure 4. TIC chromatogram of GC/MS analysis of Raleigh sludge -- spiked and methylated with diazomethane.

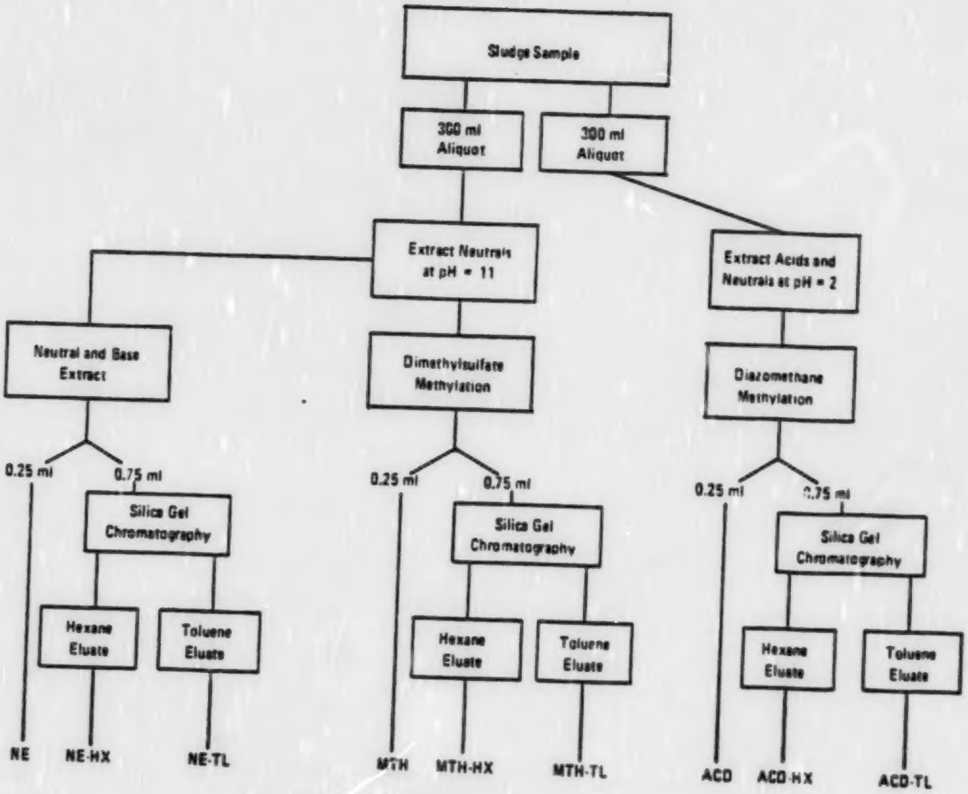

Sludge Sample
300 ml Aliquot
300 ml Aliquot
Extract Neutrals at pH = 11
Extract Acids and Neutrals at pH = 2
Neutral and Base Extract
Dimethylsulfate Methylation
Diazomethane Methylation
0.25 ml
0.75 ml
Silica Gel Chromatography
Hexane Eluate
Toluene Eluate
NE
NE-HX
NE-TL
0.25 ml
0.75 ml
Silica Gel Chromatography
Hexane Eluate
Toluene Eluate
MTH
MTH-HX
MTH-TL
0.25 ml
0.75 ml
Silica Gel Chromatography
Hexane Eluate
Toluene Eluate
ACD
ACD-HX
ACD-TL

Figure 5. Flow diagram of sample extraction and workup procedure.

Table 3. COMPOUNDS IDENTIFIED IN SPIKED RALEIGH SLUDGE AFTER METHYLATION WITH DIAZOMETHANE

Compound	Retention Time (min)
2-chloro-5-methoxyphenol	0.54
2-chloro-1,5-dimethoxybenzene	0.79
methyl-2,3,6-trichlorophenylacetate (methyl-Fenac)	2.74
pentachloroanisole (methyl-PCP)	3.84
methyl-2,4,5-trichlorophenoxyacetate (methyl-245-T)	4.64
3,3',5,5'-tetrachloro-4,4'-dimethoxybiphenyl	12.64

Table 4. PARENT, MID, AND "DOUBLE" MID IONS FOR PCBS

Compound	M	M + 2	M + 4	MID Ions	"Double" MID Ions	
$C_{12}H_9Cl$	188	190	192	188	188	190
$C_{12}H_8Cl_2$	222	224	226	222	222	224
$C_{12}H_7Cl_3$	256	258	260	256	256	258
$C_{12}H_6Cl_4$	290	292	294	292	290	294
$C_{12}H_5Cl_5$	324	326	328	326	324	328
$C_{12}H_4Cl_6$	358	360	362	360	358	362
$C_{12}H_3Cl_7$	392	394	396	394	394	398
$C_{12}H_2Cl_8$	426	428	430	430	428	432
$C_{12}HCl_9$	460	462	464	464	464	468
$C_{12}Cl_{10}$	494	496	498	498	496	500

conditions: 150° for three min, programmed to 230° at 8°/min and held isothermally until all peaks had eluted. These temperature conditions, however, were found to be too severe for adequate resolution of some of the early-eluting compounds (e.g., chlorobenzenes), so the lower initial temperature conditions were utilized.

As depicted in Figure 1, the PCBs were well-resolved and eluted within about 18 min. The lower initial temperature employed for most sample analysis was found to provide similar resolution of PCBs.

The detection limits were not specifically evaluated, but may be assumed about 50-100 ng, given the high background. This detection limit corresponded to a detection level of about 250-500 μg/ℓ of sludge.

The data output of the GC/MS was reviewed at several levels. The instrumental operator printed out TIC chromatograms and selected spectra (from about 10 to 100) which contained or appeared to contain halogen clusters. The data were then reviewed by the supervisor to assure data quality and then released for interpretation. In cases where spectra were not identifiable or had anomalous components (e.g., ion intensities differing from the theoretical isotope ratio), further data printout was obtained. This included different background subtractions, no background subtraction, printing of all spectra through a given region and ion chromatograms (plots of individual ion intensities vs. time). These techniques generally provided the necessary information to judge whether an observed isotope cluster was real or merely coincidental occurrence of ions from unrelated compounds or background. In a few instances where doubt as to the authenticity of a compound remained, the identification was labeled "tentative".

5.3.2 Quantitation of PCBs

Polychlorinated biphenyls were quantitated by GC/MS using the multiple ion detection (MID) mode to provide maximum sensitivity and precision. MID has been used successfully in similar research on polychlorinated naphthalenes.(6) Multiple ion detection is an operational mode for a quadrupole gas chromatograph/mass spectrometer where up to nine m/e values are step-jumped at short time intervals. Since this technique allows integration of ion intensity for a longer time period for the desired ions than in the customary full-scan mode, the sensitivity of the instrument is increased by approximately two orders of magnitude. By judicious selection of m/e values to be monitored, interference by unwanted compounds can usually be minimized.

Ten ions were selected for monitoring: one from the parent cluster for each of the two chlorinated biphenyls ($C_{12}H_7Cl$-$C_{12}Cl_{10}$). Although the parent ions were not necessarily the most intense, the probability of interference by PCB fragment ion or other contaminants was reduced. Ions were chosen from the M (parent), M + 2, or M + 4 m/e values (Table 4) according to an optimum combination of greatest intensity and least interference from other PCBs. Since only nine channels are available for MID analysis on the Finnigan GC/MS, each sample was run twice using different ions.

To confirm the presence of PCBs detected by MID which were not confirmed in the less-sensitive full scan mode, "double" MID analysis was used. In this technique, two ions from a parent cluster were monitored and the intensity measured compared with the theoretical isotope ratio.

The calculation of relative molar response (RMR) for the quantitation of sample components precluded the need for a calibration curve. The RMR ions calculated as the integrated peak area of a known amount of compound, A°_{unk}, with respect to the integrated peak area of a known amount of standard, A°_{std} (in this case anthracene), according to the equation

$$\mathrm{RMR} = \frac{A^{\circ}_{unk}/\mathrm{moles}_{unk}}{A^{\circ}_{std}/\mathrm{moles}_{std}} = \frac{(A^{\circ}_{unk})(mw_{unk})(g_{std})}{(A^{\circ}_{std})(mw_{std})(g_{unk})} \qquad \text{(Equation 1)}$$

From this calculated value, the concentration of an identified compound in a sample was calculated by rearranging Equation 1 to give

$$g_{unk} = \frac{(A_{unk})(mw_{unk})(g_{std})}{(A_{std})(mw_{std})(\mathrm{RMR})} \qquad \text{(Equation 2)}$$

The use of RMR for quantitation in GC/MS has proven successful in repeated application to similar research problems.(6-8)

Polychlorinated biphenyls were quantitated using an external standard and a previously determined Relative Molar Response (RMR). The standard chosen was anthracene (parent ion m/e 178), which does not interfere with PCB determination, nor do PCBs or their fragment ions interfere with the determination of anthracene.

The RMRs were measured for the available PCB isomers as shown in Table 5. A plot of RMR vs. degree of chlorination yields a non-linear relation shown in Figure 6. The points on the graph fit the equation,

$$\ell n \text{ RMR} = 0.1486 - 0.3159 \text{ (degree of chlorination)}.$$

This equation, which has a correlation coefficient of 0.9941 allows extrapolation to RMR values for hepta-, octa-, and nonachloronaphthalenes as listed in Table 5. No consideration has been given to the effect of positional isomers on the RMR values.

5.3.3 Selection of Samples for Analysis

The number of fractions generated in the extraction and cleanup steps was greater than that necessary to identify the PCBs and related compounds in each sludge sample. Initial analyses were thus directed toward determining which fractions were most likely to contain compounds of interest. The sample obtained from Philadelphia was selected for full analysis, since a preliminary analysis of its NE found a wide variety of chlorinated organics. A summary of the compounds found in the various fractions, (Table 6) illustrates the redundancy of analysis. Since the background was not prohibitive and since nearly all of the compounds found in NEHX or NETL were identified in NE, this fraction was deemed most likely to yield useful full scan GC/MS results. Accordingly all NE fractions were analyzed. This would be the fraction which would most likely contain PCBs.

It appeared from the analysis of the fractions of Philadelphia, Raleigh and other sludges that neither MTH, ACD nor their chromatographed fractions contained a significant number of identifiable compounds not already detected in the NE fraction. It was, therefore, decided that methylated fractions would be analyzed if and only if chlorinated compounds were seen in the NE fraction which contained derivitizable functionalities, or which could degrade or metabolize to acidic compounds. Since it appeared from the analysis of the Philadelphia sludge fractions that the ACD fraction would

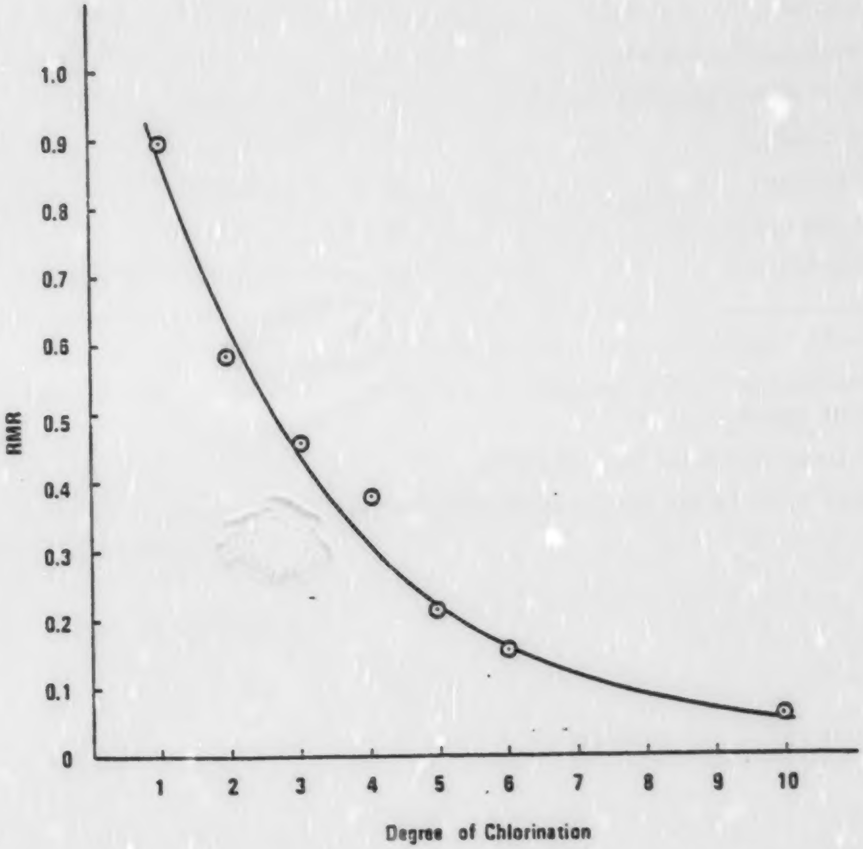


Figure 6. RMR vs. degree of chlorination for polychlorobiphenyls.

Table 5. RELATIVE MOLAR RESPONSE VALUES FOR PCBS

Compound	Degree of Chlorination	RMR[a]	SD[b]	RSD[c]
4-chlorobiphenyl	1	0.889	0.169	0.19
4,4'-dichlorobiphenyl	2	0.588	0.094	0.16
2,4',5-trichlorobiphenyl	3	0.455	0.098	0.22
2,3',5,5'-tetrachlorobiphenyl	4	0.375	0.096	0.26
2,3,4,5,6-pentachlorobiphenyl	5	0.215	0.049	0.23
2,2',4,4',5,5'-hexachlorobiphenyl	6	0.157	0.035	0.22
heptachlorobiphenyl	7	0.127[d]		
octachlorobiphenyl	8	0.0927[d]		
nonachlorobiphenyl	9	0.0676[d]		
decachlorobiphenyl	10	0.0525	0.0019	0.37

[a] Relative Molar Response, anthracene standard = 0.268 ng/μl

[b] Standard Deviation - nine values; three replicates at ∿1 ng/μl, and three at ∿50 ng/μl.

[c] Relative Standard Deviation, SD/RMR.

[d] Extrapolated from other RMR values using equation in text.

Table 6. SUMMARY OF COMPOUNDS FOUND IN FRACTIONS OF PHILADELPHIA SLUDGE EXTRACT

Retention Time (min)[a]	Compound	Bases + NE	NE-HX	NE-TL	MTH	MTH-HX	MTH-TL	Neutrals + ACD	ACD-HX	ACD-TL
0.44	dichlorobenzene							X	X	
(0.64)	mw = 187, Cl_2				X					
0.74	mw = 195, Cl_1			X				X	X	
0.83	trichlorobenzene		X					X	X	
(0.74)	tetrachlorobenzene	X	X					X	X	
2.09 (1.09)	dichloroaniline			X	X					
3.4 (1.14)	mw = 240, Cl_4	X	X					X	X	
4.1	mw = 240, Cl_4		X					X	X	
8.6-10.1 (5.8)	mw = 288, Cl_1	X		X				X		
9.6-11.1 (7.2)	dichlorobenzophenone	X								
9.9	mw = 269, Cl_1			X						
10.8	mw = 241, Cl_1									X
10.3-11.1 (8.6)	DDE	X	X	X				X	X	
12.8	mw = 356, Cl_2							X		
12.8	mw = 285, Cl_1								X	X
15.0	mw = 397, Cl_1							X		

[a] Values in parentheses are for previous GC temperature programming conditions: 150° for 5 min, 8°/min to 230°.

[b] Tentative identification. In cases where a compound is unidentified, the apparent molecular weight and apparent number of chlorines are given.

yield the most information, this fraction was selected as the methylated fraction to be analyzed first.

6.0 SAMPLING

Sludge samples were collected by EPA Regional personnel and by Research Triangle Institute from municipal wastewater treatment plants across the country.

6.1 GLASSWARE AND STORAGE

Wide-mouth, one liter glass bottles were thoroughly cleaned and heated to 500°C to remove residual organics. Duplicate sample jars with a third "blank" containing distilled water were shipped to the Regional personnel. Samples were collected, documented, and returned. Immediately upon receipt, Research Triangle Institute personnel logged in the samples, coded the container and stored tham at 5°, awaiting analysis.

6.2 SAMPLING DOCUMENTATION

Each sample was accompanied by a "Sampling Protocol Sheet" reproduced in Appendix B. This, in most cases, provided extensive documentation of the sample history.

6.3 SAMPLING DETAILS

Table 7 lists the locations of the sludge sampling cities. While most of the plants are in large metropolitan areas, they represent a variety of common wastewater treatment processes and a variety of sludge sample characteristics.

The sample collected at the New Bedford, Massachusetts wastewater treatment plant (NBM), a primary treatment plant, was of a fluid consistency. The sludge had been thickened and centrifuged prior to sampling. Aerovox Corporation and Cornell Dubilier were listed by EPA Region I personnel as potential PCB sources.

The sample collected at the Northeast Sewage Treatment Plant in Philadelphia, Pennsylvania (PH) was collected from an anaerobic digester.

Table 7. SUMMARY OF SEWAGE SLUDGE SAMPLE COLLECTION

Region	Municipality	Location	Site
I	New Bedford, MA	New Bedford Wastewater Treatment Plant	Between Centrifugation and Incineration
III	Philadelphia, PA	Northeast Sewage Treatment Plant	Anaerobic Digester No. 6
IV	Raleigh, NC	Neuse River Wastewater Treatment Plant	Aerobic Digester and and Centrifuge
V	Chicago, IL	Metropolitan Sanitary District of Great Chicago-Stickney West-Southwest Plant, Cicero	No. 6 Digester
VI	Houston, TX	Sims Bayou Sludge Disposal Plant	Flash Dried Sludge
VII	Kansas City, KS	Kaw Point Sewage Treatment Plant	No. 2 Digester
VIII	Denver, CO	Denver Metropolitan Sewage Treatment Plant	Primary Digestion
IX	San Francisco, CA	SE San Francisco Water Pollution Control Plant	After Digestion and Elutriation
X	Seattle, WA	Metro West Point	Secondary Digester

The digesters were sour at the time of collection. Personnel from EPA Region III listed Allied Chemical, Philadelphia, Pennsylvania and Rohm and Haas Company, Bristol, Pennsylvania as suggested sources of chlorinated hydrocarbons in the sludge.

The Neuse River Wastewater Treatment Plant serving Raleigh, North Carolina, (RAH) a new, modern plant. At the time that sludge samples were collected from the aeration pond, the sludge digestion system had not yet equilibrated. Samples were also collected directly from a centrifuge.

The West-Southwest Sewage Treatment Plant of the Metropolitan Sanitary District of Greater Chicago in Cicero, Illinois (CHI) is the world's largest sewage treatment plant, according to sampling documentation supplied with the sample collected by EPA Region V personnel. The sample was collected from an anaerobic digester and is of particular interest since the dried sludge is distributed as an organic fertilizer, "Nu-Earth".

The sludge sample collected by EPA Region VI personnel at the Sims Bayou Sludge Disposal Plant, Houston, Texas (HOU) was a dried granular sample. The sludge at this plant is floculated, vacuum filtered, and dried at 1000-1200°F in a cyclone, making an average of ten passes through the dryer.

The Kaw Point Sewage Treatment Plant serves the Kansas City, Kansas metropolitan area (KC). A sample was collected from a digester (type unspecified) by EPA Region VII personnel.

A sample collected at the Denver, Colorado Metro Sewage Treatment Plant (DN) was taken from the primary digestion pipe. The sample had been pumped from another plant approximately three km to the north.

A sample was collected at the Southeast San Francisco Water Pollution Control Plant (SF) by EPA Region IX personnel. The sample was collected after the elutriation tanks and before the filters. This plant serves a heavily industrialized area and also receives sludge and scum directly from the North Point Plant, serving a mostly residential area.

EPA Region X personnel collected a sample at the Metro West Point Treatment Plant, Seattle, Washington (SEA). The sample was taken at the intermediate level drained off from a completely mixed secondary digestion. According to EPA Region X personnel, Seattle City Light and Puget Sound Power and Light have previously been sources of PCBs in the sewage system.

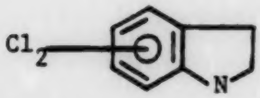
7.0 ANALYSIS FOR CHLORINATED COMPOUNDS IN SLUDGE SAMPLES

The results of the sample analysis are summarized in Table 8. A total of 35 compounds were found in sewage sludge, although not all compounds could be identified. In cases where a compound was identified, but no standard was available for retention time comparison, the identification was labeled "tentative". Where a reasonable structure or formula may be proposed to fit the data, this was done in the text. In some cases where the spectral quality was insufficient to definitely assign a molecular weight and/or chlorine content to an unidentified compound, it was labeled as "tentative". It must be noted that a large number of spectra contained what appeared to be chlorine isotope clusters which are not reported. This could be due to interferences, very low levels, or spurious peaks.

The following sections discuss in detail the results of the sludge sample analyses, arranged by city. For each fraction analyzed, the TIC chromatogram and a table of compounds found are presented. Mass spectra of each compound found are presented in Appendix C.

7.1 RESULTS OF ANALYSIS OF NEW BEDFORD SLUDGE

The neutral and diazomethane-methylated extract of NBM sludge were analyzed, the compounds found in these samples are listed in Tables 9 and 10, respectively. The compound with mw = 189 and two chlorines found in the diazomethane-methylated extract may have the molecular formula $C_8H_7NCl_2$, in which case it could be a dichloro-dihydroindole or related compound, for example:



The identification of dichloronaphthalene remains tentative because the retention times of the unknown (3.7 min) and standard (6.7 min) differ markedly and since the unknown eluted so much earlier than the corresponding biphenyl

Table 8. SUMMARY OF CHLORINATED COMPOUNDS FOUND IN SEWAGE SLUDGE

Compound[a]	Retention Time (min)[b]	Number of Times Observed[c]
dichlorobenzene	0.5	2
mw = 195, Cl_1	0.8	3
mw = 221, Cl_1	0.9	1
trichlorobenzene	1.0	6
chloroaniline (tent.)	1.2	1
dichloroaniline	2.1-4.7 (1.1)	5
tetrachlorobenzene	2.2 (0.7)	6
mw = 187, Cl_2	2.3-2.7 (0.6)	7
mw = 171, Cl_2	3.0	2
mw = 240, Cl_4[e]	3.0, 4.3 (1.1)	6
trichloroaniline[d]	3.2, 4.4	2
dichloronaphthalene	3.7	1
trichlorophenol	3.7	2
mw = 302, Cl_1	4.5	1
mw = 210, Cl_3	5.1	1
chlorobiphenyl	6.2	1
dichlorobiphenyl[f]	6.3-8.2	2
trichlorobiphenyl[f]	7.5-9.6	3
mw = 192, Cl_1	7.6	1
mw = 288, Cl_1	8.6-11.1 (5.8)	3
tetrachloronaphthalene	8.6	1
mw = 218, Cl_1 (tent.)	9.1	1
mw = 256, Cl_1	9.1	1
tetrachlorobiphenyl[f]	9.3-10.2	2
dichlorobenzophenone	9.2 (7.2)	2
mw = 269, Cl_1	9.9	1
mw = 256, Cl_2	10.1	1
pentachlorobiphenyl[f]	10.2-11.1	1

Table 8. (Cont'd)

Compound	Retention Time (min)[a]	Number of Times Observed[b]
mw = 288, Cl_3	10.5	2
mw = 280, Cl_1	10.7	1
mw = 241, Cl_1	10.8	1
mw = 285, Cl_1	12.6	2
DDE[e]	12.7, 13.2 (8.6)	7
mw =356, Cl_2	12.8	1
mw = 397, Cl_1	15.0	1

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorines. If the identification of some compounds is tentative, they are denoted by (tent.)

[b] Retention times are listed for the chromatographic temperature conditions, 120° for 3 min, then 12°/min to 230°, then hold. Values in parentheses are for chromatographic temperature conditions, 150° for 3 min, then 8°/min to 230, then hold.

[c] The number of samples out of 24 total in which this compound was observed.

[d] Differences in retention times indicates possibly different isomers.

[e] Two separate isomers observed in some samples.

[f] Several isomers observed.

Table 9. HALOGENATED COMPOUNDS FOUND IN NEUTRAL EXTRACT OF NEW BEDFORD SLUDGE

Compound	Retention Time (min)[a]
trichlorobenzene	1.0
trichloroaniline	3.2
dichlorobiphenyl	6.3 - 8.2
trichlorobiphenyl	7.5 - 9.6
tetrachlorobiphenyl	9.3 - 10.2
pentachlorobiphenyl	10.2 - 11.1

[a] See Figure 7 for TIC chromatogram.

Table 10. CHLORINATED COMPOUNDS FOUND IN DIAZOMETHANE METHYLATED EXTRACTS OF NEW BEDFORD SLUDGE

Compound[a]	Retention Time (min)[b]
mw = 187, Cl_2	2.6
dichloronaphthalene (tent.)	3.7
trichloroaniline	4.4
chlorobiphenyl	6.2
dichlorobiphenyl	7.2 - 7.9
trichlorobiphenyl	8.4 - 9.2
tetrachloronaphthalene	8.6
tetrachlorobiphenyl	9.2 - 10.0

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorines.

[b] See Figure 8 for TIC chromatogram.

compounds. Previous experience(6), however, has shown that the different positional isomers among the polychlorinated naphthalenes (as well as PCBs) can have widely different retention times. In addition, polychlorinated naphthalenes have been identified(6) in environmental samples obtained from this area, so their presence in sludge is not surprising.

The PCB concentrations in the neutral extract of NBM sludge was judged sufficient to warrant quantitation. Therefore, the hexane eluate of that fraction was submitted to GC/MS analysis in the MID mode for quantitation. This fraction was used to reduce the interferences. Figure 7 shows the MID chromatograms for the lower PCB isomers, clearly illustrating their presence. It should be noted that fragments of higher isomers are observed at longer retention times in the channel for a lower isomer; for instance, fragments of trichlorobiphenyls may be observed between 7.7-10 min in the monochlorobiphenyl chromatogram. The compounds found in this analysis and their retention times are listed in Table 11. The quantitative results are shown in Table 12.

7.2 RESULTS OF ANALYSIS OF PHILADELPHIA SLUDGE

All nine fractions of the PH sludge samples were analyzed. The compounds found in each fraction are listed in Tables 13-19 and summarized in Table 6. The hexane and toluene eluates of the dimethylsulfate-methylated fraction did not contain any detectable chlorine-containing compounds. The two compounds with molecular weight of 240 and four chlorines appear to be isomers of $C_8H_4Cl_4$ which may be tetrachlorostyrene. This identification is plausible since chlorostyrenes (hexa-through octa-) have been observed in Great Lakes water samples.(9) Unfortunately, an authentic sample was not available for correlation of retention times. The dichlorobenzophenone identified in the neutral and diazomethane-methylated fractions was confirmed by comparison of the retention time with an authentic sample (4,4'-dichlorobenzophenone). In some of the fractions (e.g., the hexane eluate of the neutral extract), two peaks were identified as DDE isomers which are assumedly the two common isomers, o,p'-DDE [1,1-dichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)ethylene] and p,p'-DDE [1,1-(dichloro-2,2-bis(p-chlorophenyl)ethylene] which generally are separable by GC.

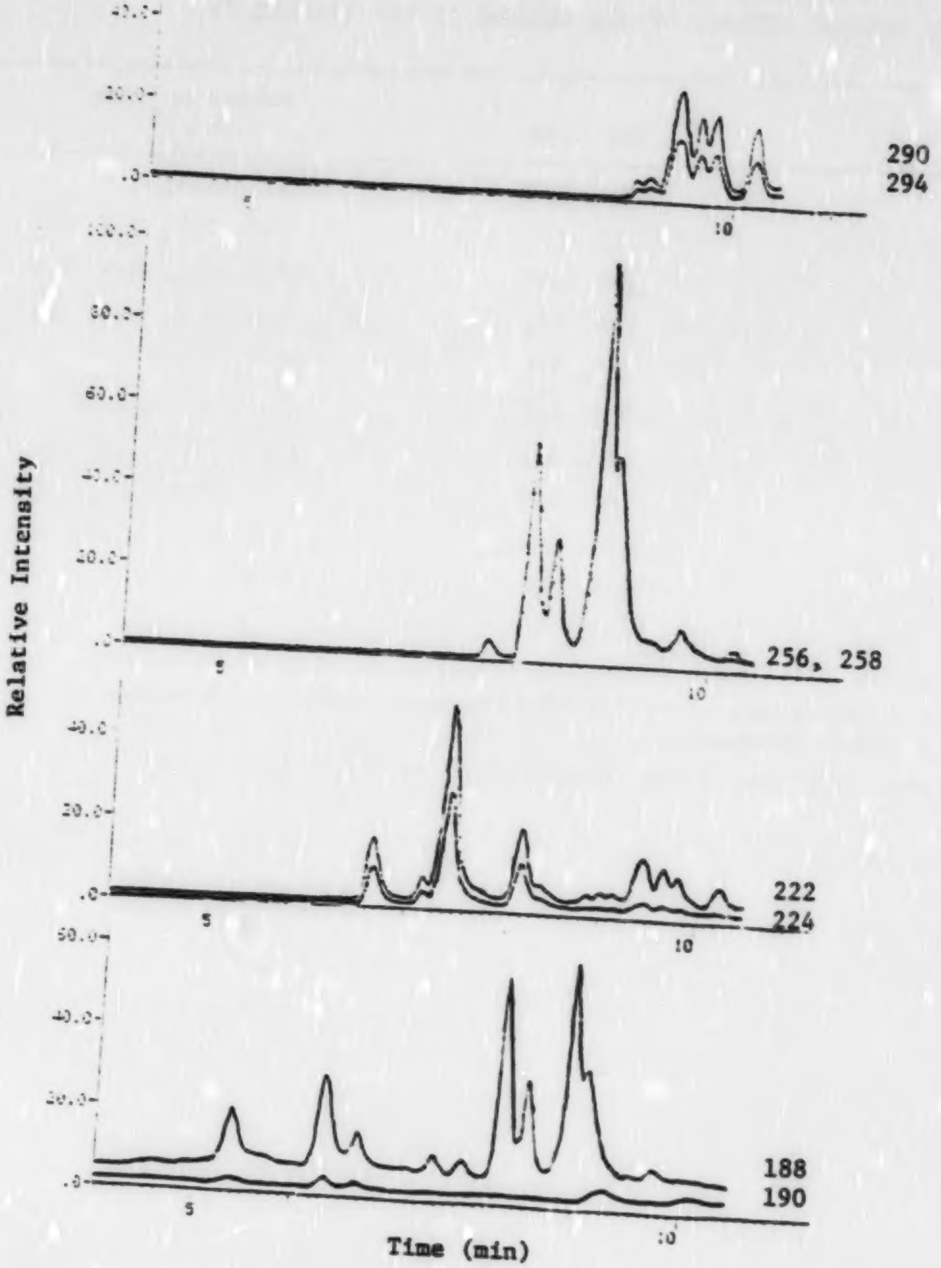


Figure 7. MID chromatograms illustrating PCBs in hexane eluate of neutral extract of NBM sludge.

(Theoretical ratios: 290/294 = 100/64, 256/258 = 100/98, 222/224 = 100/65, 188/190 = 100/32).

Table 11. RETENTION TIMES OF PCBS FOUND IN HEXANE ELUATE OF NEUTRAL EXTRACT OF NEW BEDFORD SLUDGE (FIGURE 7)

Compound[a]	MID IONS	Retention Time (min)[b]
$C_{12}H_9Cl$	188, 190	5.3, 6.3, 6.7
$C_{12}H_8Cl_2$	222, 224	6.7, 7.5, 8.2
$C_{12}H_7Cl_3$	256, 258	7.8, 8.2, 8.5, 8.9
$C_{12}H_6Cl_4$	290, 294	9.0, 9.5, 9.7, 9.8, 10.2
$C_{12}H_5Cl_5$	324, 328	10.2, 11.0
$C_{12}H_4Cl_6$	358, 362	11.4, 11.7, 12.0
$C_{12}H_3Cl_7$	394, 398	13.0
$C_{12}H_2Cl_8$	428, 432	--
$C_{12}HCl_9$	464, 468	--
$C_{12}Cl_{10}$	496, 500	15.4
Anthracene	(std), 179	8.1

[a] Confirmed by comparison of retention time with standard and ratios of chlorine isotopic abundance.

[b] GC conditions: 120° for 3 min, then 12°/min to 230°, then hold.

Table 12. QUANTITATION OF PCBs IN HEXANE ELUATE OF NEUTRAL EXTRACT OF NEW BEDFORD SLUDGE

Compound	Amount Found (µg/ml)	Sludge Concention (µg/ℓ)
$C_{12}H_9Cl$	8.5[a]	57
$C_{12}H_8Cl_2$	220[a]	1500
$C_{12}H_7Cl_3$	760[a]	5100
$C_{12}H_6Cl_4$	470[a]	3100
$C_{12}H_5Cl_5$	57	380
$C_{12}H_4Cl_6$	76	510
$C_{12}H_3Cl_7$	24	160
$C_{12}H_2Cl_8$	-	-
$C_{12}HCl_9$	-	-
$C_{12}Cl_{10}$	14	93
Total PCBs	1600	10,800

[a] Average of two determinations

Table 13. CHLORINATED COMPOUNDS FOUND IN NEUTRAL EXTRACT OF PHILADELPHIA SLUDGE

Compound[a]	Retention Time (min)[b]
tetrachlorobenzene	0.7
mw = 240, Cl_4	1.1
mw = 288, Cl_1	5.8
dichlorobenzophenone	7.2
DDE	8.6

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

[b] Note: gas chromatographic conditions are 150° for 3 min, then 8°/min to 230° and then held at the upper limit.

Table 14. CHLORINATED COMPOUNDS FOUND IN HEXANE ELUATE OF NEUTRAL EXTRACT OF PHILADELPHIA SLUDGE

Compound[a]	Retention Time (min)
trichlorobenzene	0.8
tetrachlorobenzene	2.6
mw = 240, Cl_4	3.0
mw = 240, Cl_4	4.3
DDE	12.7
DDE	13.2

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

Table 15. CHLORINATED COMPOUNDS FOUND IN TOLUENE ELUATE OF NEUTRAL EXTRACT OF PHILADELPHIA SLUDGE

Compound[a]	Retention Time (min)
mw = 195, Cl_1	0.7
dichloroaniline	2.1
mw = 288, Cl_1	9.5 - 10.1
mw = 269, Cl_1	9.9
DDE	13.0

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

Table 16. CHLORINATED COMPOUNDS FOUND IN DIMETHYLSULFATE-METHYLATED EXTRACT OF PHILADELPHIA SLUDGE

Compound[a]	Retention Time (min)[b]
mw = 187, Cl_2	0.5
dichloroaniline	1.1

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

[b] Note: gas chromatographic conditions are 150° for 3 min, then 8°/min to 230° and then held at the upper limit.

Table 17. CHLORINATED COMPOUNDS FOUND IN DIAZOMETHANE-METHYLATED FRACTION OF PHILADELPHIA SLUDGE

Compound[a]	Retention Time (min)
dichlorobenzene	0.5
mw = 195, Cl_1	0.8
trichlorobenzene	1.0
tetrachlorobenzene	2.2
mw = 240, Cl_4	3.6
mw = 240, Cl_4	4.6
mw = 288, Cl_1	8.6
dichlorobenzophenone	9.6
DDE	10.5 - 10.9
mw = 356, Cl_2	12.8
mw = 397, Cl_1	15.0

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

Table 18. CHLORINATED COMPOUNDS FOUND IN HEXANE ELUATE OF DIAZOMETHANE-METHYLATED EXTRACT OF PHILADELPHIA SLUDGE

Compound[a]	Retention Time (min)
dichlorobenzene	0.5
mw = 195, Cl_1	0.9
trichlorobenzene	1.1
tetrachlorobenzene	2.4
mw = 240, Cl_4	4.1
mw = 240, Cl_4	5.2
DDE	11.1 - 11.2
mw = 285, Cl_1	12.8

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

Table 19. CHLORINATED COMPOUNDS FOUND IN TOLUENE ELUATE OF DIAZOMETHANE-METHYLATED EXTRACT OF PHILADELPHIA SLUDGE

Compound[a]	Retention Time (min)
mw = 241, Cl_1	10.8
mw = 285, Cl_1	12.6

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

7.3 RESULTS OF ANALYSIS OF RALEIGH SLUDGE

The neutral, diazomethane-methylated, and hexane eluate of the diazomethane-methylated extracts of RAH sludge were analyzed. The chlorinated compounds found in these samples are listed in Tables 20-22, respectively.

As mentioned previously, the tetrachloro- compounds with mw = 240 are probably tetrachlorostyrene isomers. The dichloro- compound with a molecular weight of 187 may have a molecular formula of $C_8H_7NCl_2$ (Fig. C-56).

7.4 RESULTS OF ANALYSIS OF CHICAGO SLUDGE

The hexane eluate of the neutral extract of CHI sludge was analyzed. The neutral extract portion which was not liquid chromatographed was too viscous for direct GC/MS analysis. No chlorinated compounds were found in the fraction analyzed, so no further fractions were analyzed.

7.5 RESULTS OF ANALYSIS OF HOUSTON SLUDGE

The neutral and diazomethane-methylated extracts of HOU sludge were analyzed. The chlorinated compounds found in these samples are listed in Tables 23 and 24, respectively. The dichloro- compound, mw = 187, may have a molecular formula of $C_8H_7NCl_2$ (Fig. C-67). The fragmentation pattern (Fig. C-71) of the compound with molecular weight 256 and one chlorine found in the diazomethane-methylated fraction repeatedly loses 32 mass units, indicating losses of O_2 or S.

7.6 RESULTS OF ANALYSIS OF KANSAS CITY SLUDGE

The neutral and diazomethane-methylated fractions of KC sludge were analyzed. The chlorinated compounds in the samples are listed in Tables 25 and 26, respectively. The dichloro- compounds, mw = 187 may have a molecular formula of $C_8H_7NCl_2$ (Fig. C-78).

7.7 RESULTS OF ANALYSIS OF SAN FRANCISCO SLUDGE

The neutral extract of SF sludge was analyzed. Since only one chlorinated compound was found (Table 29), the other fractions were not analyzed.

7.8 RESULTS OF ANALYSIS OF SEATTLE SLUDGE

The neutral extract of SEA sludge was analyzed. Since only two chlorinated compounds were found (Table 30), the other fractions were not analyzed. The compound containing two chlorines, mw = 187, may have the molecular formula $C_8H_7NCl_2$.

Table 20. CHLORINATED COMPOUNDS FOUND IN NEUTRAL EXTRACT OF RALEIGH SLUDGE

Compound[a]	Retention Time (min)
mw = 221, Cl_1	0.9
chloroaniline (tent.)	1.2
mw = 187, Cl_2	1.9
dichloroaniline	3.5

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

Table 21. CHLORINATED COMPOUNDS FOUND IN DIAZOMETHANE-METHYLATED EXTRACT OF RALEIGH SLUDGE

Compound[a]	Retention Time (min)[b]
tetrachlorobenzene	0.7
mw = 240, Cl_4	1.2
mw = 302, Cl_1	4.5
DDE	8.8
DDE	9.7

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

[b] Note: gas chromatographic conditions are 150° for 3 min, then 8°/min to 230, then held at the upper limit.

Table 22. CHLORINATED COMPOUNDS FOUND IN HEXANE ELUATE OF DIAZOMETHANE-METHYLATED EXTRACT OF RALEIGH SLUDGE

Compound[a]	Retention Time (min)
tetrachlorobenzene	2.4
mw = 240, Cl_4	4.2
mw = 240, Cl_4	5.1
DDE	11.0

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

Table 23. CHLORINATED COMPOUNDS FOUND IN NEUTRAL EXTRACT OF HOUSTON SLUDGE

Compound[a]	Retention Time (min)
mw = 187, Cl_2	2.7
dichloroaniline	4.7
mw = 288, Cl_3	10.5

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

Table 24. CHLORINATED COMPOUNDS FOUND IN DIAZOMETHANE-METHYLATED EXTRACT OF HOUSTON SLUDGE

Compound[a]	Retention Time (min)
mw = 192, Cl_1	7.6
mw = 256, Cl_1	9.2
mw = 280, Cl_1	10.7

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

Table 25. CHLORINATED COMPOUNDS FOUND IN NEUTRAL EXTRACT OF KANSAS CITY SLUDGE

Compound[a]	Retention Time (min)[b]
mw = 271, Cl_2 (tent.)	3.0
trichlorophenol	3.7
dichloroaniline (tent.)	4.6
mw = 210, Cl_3	5.1
trichlorobiphenyl	9.8

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

Table 26. CHLORINATED COMPOUNDS IN DIAZOMETHANE-METHYLATED EXTRACT OF KANSAS CITY SLUDGE

Compound[a]	Retention Time (min)
mw = 187, Cl_2	2.4
mw = 171, Cl_2	2.7
trichlorophenol	3.4

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

Table 27. CHLORINATED COMPOUND FOUND IN NEUTRAL EXTRACT OF DENVER SLUDGE

Compound[a]	Retention Time (min)
mw = 288, Cl_3	11.1

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

Table 28. CHLORINATED COMPOUNDS FOUND IN DIAZOMETHANE-METHYLATED EXTRACT OF DENVER SLUDGE

Compound[a]	Retention Time (min)
trichlorobenzene	1.2
mw = 187, Cl_2	2.3
mw = 218, Cl_1 (tent.)	9.1

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

Table 29. CHLORINATED COMPOUND FOUND IN NEUTRAL EXTRACT OF SAN FRANCISCO SLUDGE

Compound[a]	Retention Time (min)
mw = 256, Cl_2	10.1

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

Table 30. CHLORINATED COMPOUNDS FOUND IN NEUTRAL EXTRACT OF SEATTLE SLUDGE

Compound[a]	Retention Time (min)
trichlorobenzene	2.0
mw = 187, Cl_2	2.5

---

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorine atoms.

7.9 RESULTS OF ANALYSIS OF DISTILLED WATER BLANK

Distilled water blanks (1 ℓ) were sent along with the sample jars to each sampling city and returned with the samples. The blank from pH was extracted and analyzed. No chlorinated compounds were found. There was no reason to believe that any other samples had been contaminated, so their blanks were not analyzed.

8.0 REFERENCES

1. National Conference on Polychlorinated Biphenyls, November 19-21, 1975, Chicago, IL. EPA 560/6-75-004 (PB 253 248).
2. O. Hutzinger, S. Safe, and V. Zitko, "The Chemistry of PCB's", CRC Press, Cleveland, 269 pp, 1974.
3. L. H. Keith, Environ. Sci. Technol., 10, 555 (1976).
4. L. H. Keith, "Analysis of Organic Compounds in Two Kraft Mill Wastewaters", EPA-600/4-75-005 (1975).
5. L. H. Keith, "Identification and Analysis of Organic Pollutants in Water", L. H. Keith, Ed. Ann Arbor Science, Ann Arbor, MI, 1976, Chapter 36.
6. M. D. Erickson, R. A. Zweidinger, L. C. Michael and E. D. Pellizzari, "Environmental Monitoring Near Industrial Sites: Polychlorinated Naphthalenes", EPA Contract No. 68-01-1978, Task I Final Report, 1977 submitted.
7. E. D. Pellizzari, "Analysis of Organic Air Pollutants By Gas Chromatography and Mass Spectroscopy", Publication No. EPA-600/2-77-100, Contract No. 68-02-2262, 112 pp., June, 1977.
8. M. D. Erickson and E. D. Pellizzari, "Analysis of a Series of Samples for Polybrominated Biphenyls (PBBs)", EPA Contract No. 68-01-1978, Task 5 Final Report, 1977, submitted.
9. D. W. Kuehl, W. L. Kopperman, G. D. Veith, and G. E. Glass, Bull. Environ. Contamin. Toxicol., 16, 127 (1976).

APPENDIX A: PROCEDURES USED TO EXTRACT, DERIVATIZE, AND CLEAN-UP SLUDGE SAMPLES FOR ANALYSIS

Table A-1. PROCEDURE FOR EXTRACTION OF NEUTRAL ORGANICS FROM SLUDGE SAMPLES

1. Adjust pH to 11 with NaOH.
2. In separatory funnel, shake sample (~300 ml)* 10 minutes with 80 ml chloroform.
3. Drain off chloroform.
4. Repeat Steps 1 and 2 successively with 70, 50, 25, 25 and 100 ml of chloroform (total extract volume ca. 350 ml).
5. Add Na_2SO_4 to $CHCl_3$ fraction to remove H_2O.
6. Vacuum filter $CHCl_3$ fraction through Whatman No. 50 filter paper to remove gross particulate matter.
7. Reduce volume of $CHCl_3$ fraction in Kuderna-Danish apparatus, followed by nitrogen blowdown to 2.0 ml.

*For dilute sludge samples. Very viscous, solid or dried samples were extracted after addition of sufficient water of a smaller aliquot to make the same consistency as the dilute sample.

Reference: Adapted from L. H. Keith, "Analysis of Organic Compounds in Two Kraft Mill Wastewaters", EPA-600/4-75-005 (1975).

Table A-2. COLUMN CLEAN-UP PROCEDURE

1. Silica gel (Davison Chemical Division, W. A. Grace, Baltimore, MD), grade 923 (100-200 mesh) washed with toluene, followed by hexane, dried at 130° for 16 hour and stored in sealed amber bottle.
2. Using 1.0 x 30 cm glass column, pack with a plug of glass wool, add silica gel in a hexane slurry to 10 cm height, and top with 1.0 cm Na_2SO_4.
3. Wash column with 50 ml hexane to settle the bed and clean any residual contaminants.
4. Save a 0.25 ml aliquot of the 2.0 ml sample, and transfer the other 1.75 ml to the column with washing.
5. Elute the PCBs with 50 ml hexane.
6. Other compounds, including pesticides are eluted with 50 ml of toluene.
7. Concentrate hexane eluate in Kuderna-Danish apparatus, followed by nitrogen blowdown to <1.9 ml.
8. Concentrate toluene eluate in a flat-bottomed boiling flask with an attached Snhyder column, followed by nitrogen blowdown to <1.9 ml.

Reference: Adapted from D. Snyder and R. Reinert, Bull. Environ. Contamin. Toxicol., 6, 385 (1971).

Table A-3. PROCEDURE FOR DIMETHYLSULFATE METHYLATION

1. Extract the original sample to remove the neutral organics (see Table A-1). The remaining aqueous slurry is methylated in this procedure.
2. A 100 ml, three-necked (standard taper 24/40 round bottom flask), equipped with a fourth neck for a thermometer, is fitted with two pressure-equalizing addition funnels, a glass stirring rod, and a magnetic stirrer.
3. Nitrogen is introduced into the top of the first addition funnel and exits from the top of the second one. Place 40 ml of Eastman reagent grade dimethylsulfate into the first addition funnel and a 50% solution of sodium hydroxide into the second.
4. Pour the sample (see Step 1) into the flask and flush the system with nitrogen.
5. After raising the temperature to 85°C, begin dropwise addition of both the dimethylsulfate and the sodium hydroxide solution. Maintain temperature between 80 and 90°C, and the pH between 10.5 and 11. Since dimethylsulfate is not readily soluble in water vigorous stirring must be used. The addition time is about one hour.
6. After all the dimethylsulfate is added, maintain the reaction vessel at 85-90°C for an additional 15-20 minutes and then cool to room temperature.
7. Add 5 ml concentrated ammonium hydroxide to destroy excess dimethylsulfate, and re-extract according to procedure for neutral organics (Table A-1).
8. Column clean-up (see Table A-2).

Note: Dimethylsulfate is a suspected carcinogen. Appropriate precautions and safety procedures should be maintained.

Reference: Adapted from L. H. Keith, "Analysis of Organic Compounds in Two Kraft Mill Wastewaters", EPA-660/4-75-005 (1975).

Table A-4. PROCEDURE FOR DIAZOMETHANE-METHYLATION

1. Bring an original 300 ml aliquot of the sample to pH 2 with ~10% H_2SO_4.
2. Extract with chloroform according to procedure for neutral organics, deleting Step 1.
3. Blowdown sample in chloroform just to dryness and suspend in ~0.5 ml anhydrous ethyl ether.
4. Add 1 ml diazomethane in ether [prepared according to Fales, H. M., *et al*., Anal. Chem., *45*, 2302 (1973)] and stopper the sample for one hour.
5. Allow the esterified sample to stand unstoppered for 1.5 hour to allow excess diazomethane to escape from the ether solution into the fume hood.
6. Bring volume to 2.0 ml.
7. Column clean-up (see Table A-2).

Note: The N-methyl-N'-nitro-N-nitrosoguanidine used to generate the diazomethane is a carcinogen. All work with this compound must be done in a carcinogenic substances laboratory and appropriate precautions taken.

Reference: Adapted from L. H. Keith, "Analysis of Organic Compounds in Two Kraft Mill Wastewaters", EPA-660/4-75-005 (1975).

Table A-5. PREPARATION OF SAMPLES FOR GC/MS ANALYSIS

1. External standard (53.6 μg anthracene) is added to each fraction (<1.9 ml volume) and the volume adjusted to 2.0 ml. The concentration of anthracene is thus 26.8 ng/μl.
2. Samples were stored at 5°C in teflon-lined screw cap vials until analysis by GC/MS as described elsewhere.

APPENDIX B: SAMPLING PROTOCOL SHEET

SAMPLING PROTOCOL SHEET

Sewage Sludge Samples (31U-1277-4)

Date and Time Collected: ____________________

Site (Full Name of Plant): ____________________

Address: ____________________

____

____

Collection Location (Digestion #, Lagoon #, etc): ____________________

Name of Person Collecting Sample: ____________________

Please describe the sewage plant in general and/or provide a diagram if available. Also please outline the area served by this plant.

Please list the treatment steps which preceed collection of the sample:

Please list any known or suspected sources of chlorinated hydrocarbons which may contribute to this sample and any suspected compounds.

Please add any comments which would further aid in characterization of this sample.

APPENDIX C: MASS SPECTRA OF CHLORINATED COMPOUNDS FOUND IN MUNICIPAL SEWAGE SLUDGE SAMPLES

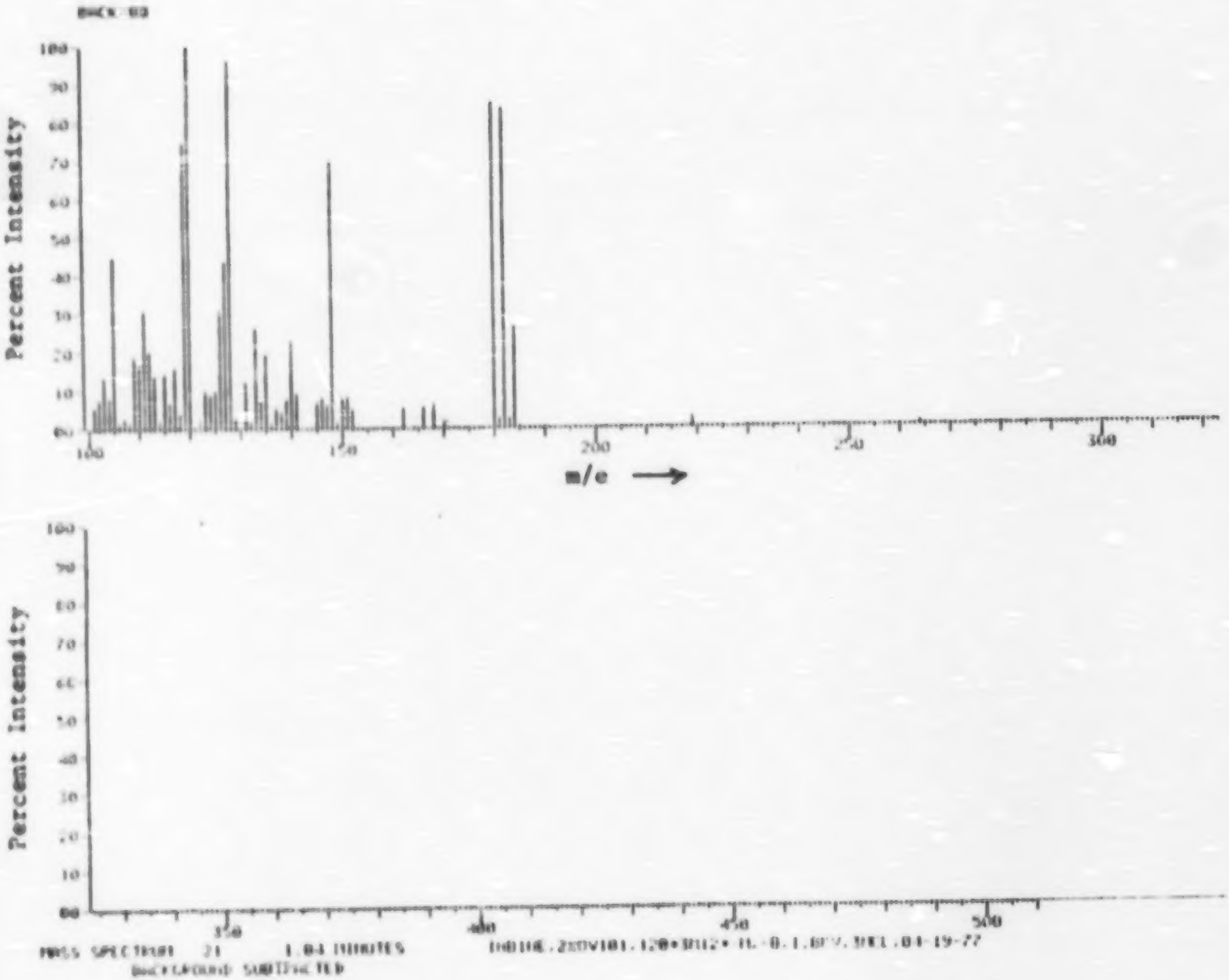


Figure C-1. Mass spectrum of trichlorobenzene (M = 180) identified in neutral extract of New Bedford sludge.

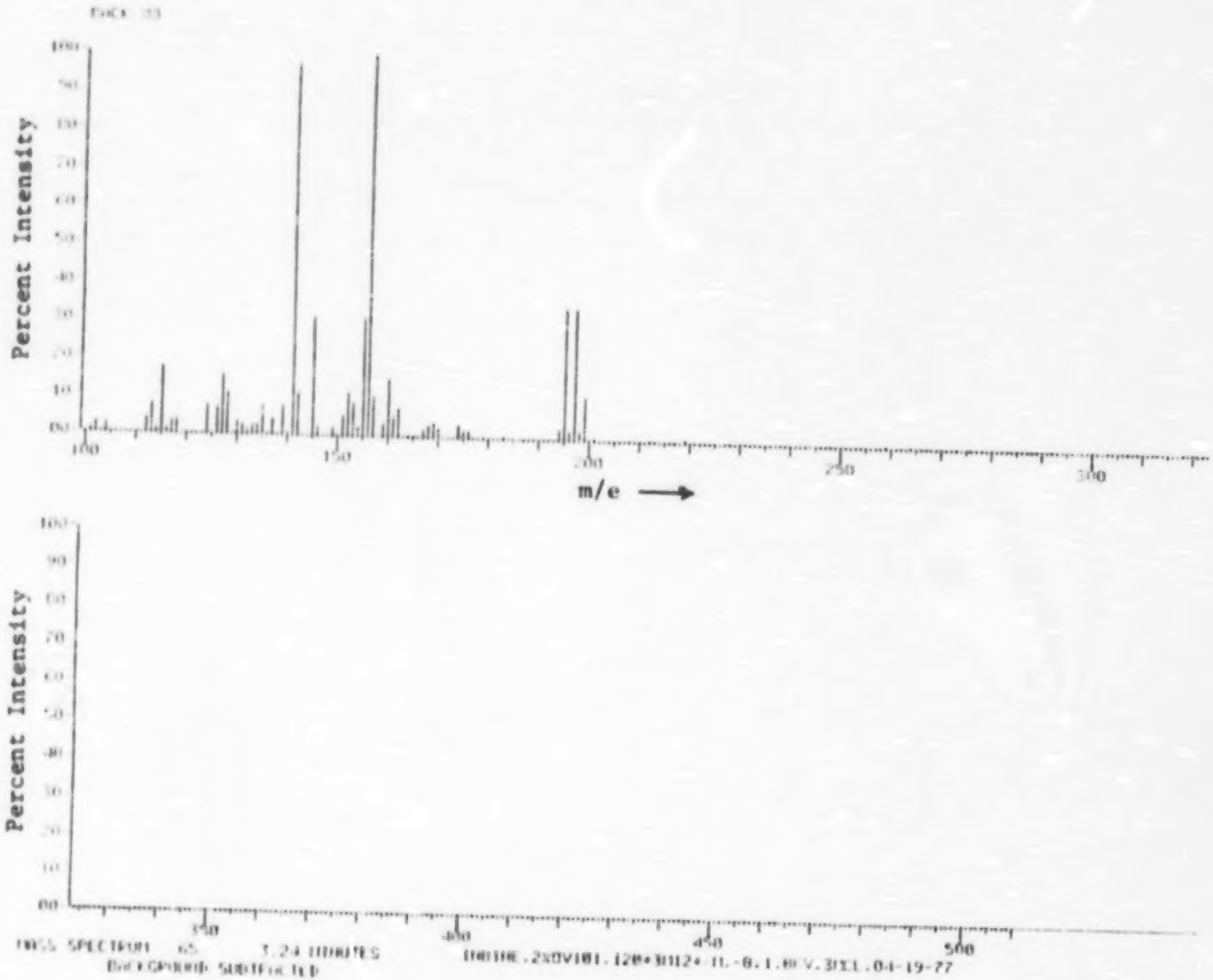


Figure C-2. Mass spectrum of trichloroaniline (M = 195) identified in neutral extract of New Bedford sludge.

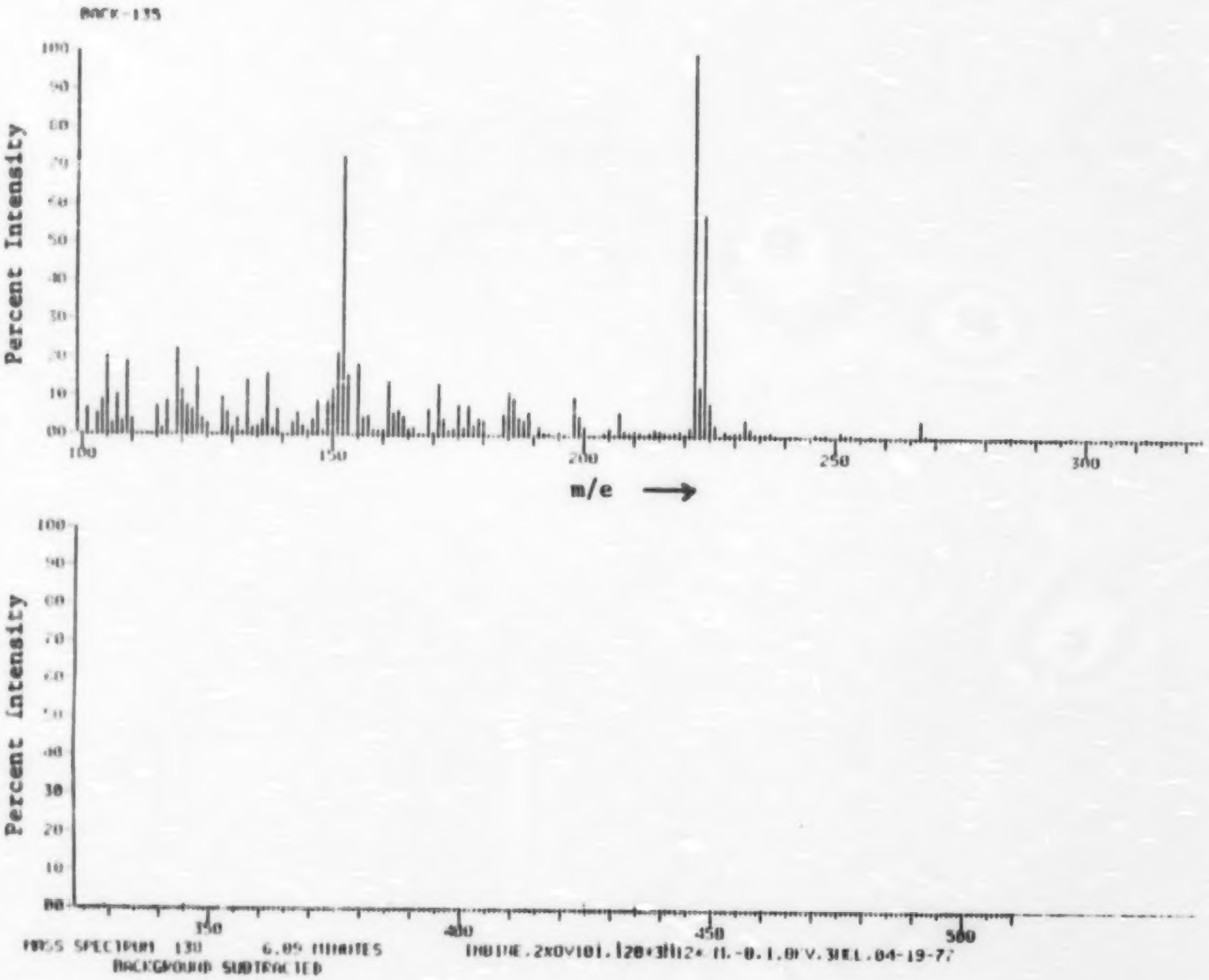


Figure C-3. Mass spectrum of dichlorobiphenyl (M = 222) identified in neutral extract of New Bedford sludge.

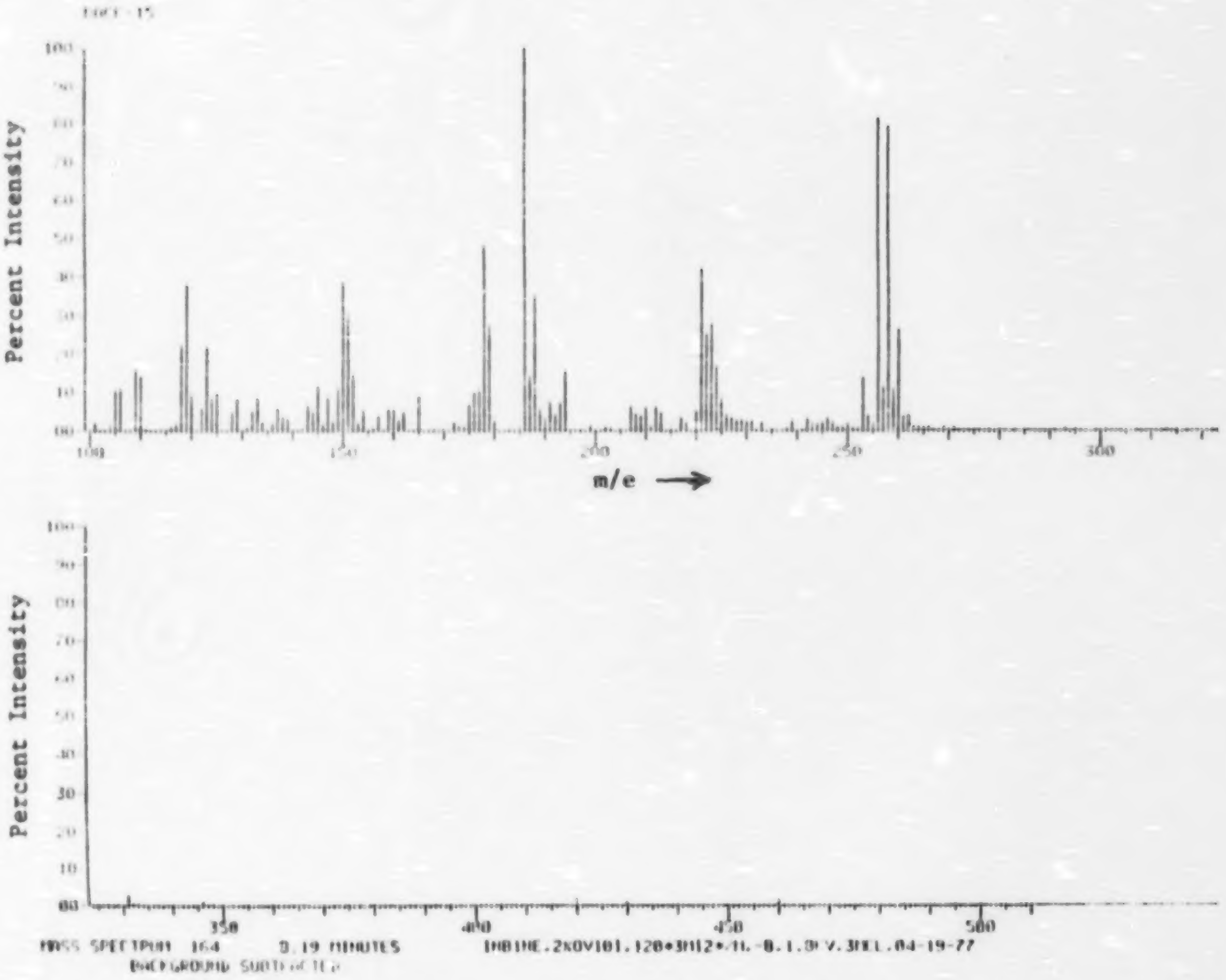


Figure C-4. Mass spectrum of trichlorobiphenyl (M = 256) identified in neutral extract of New Bedford sludge.

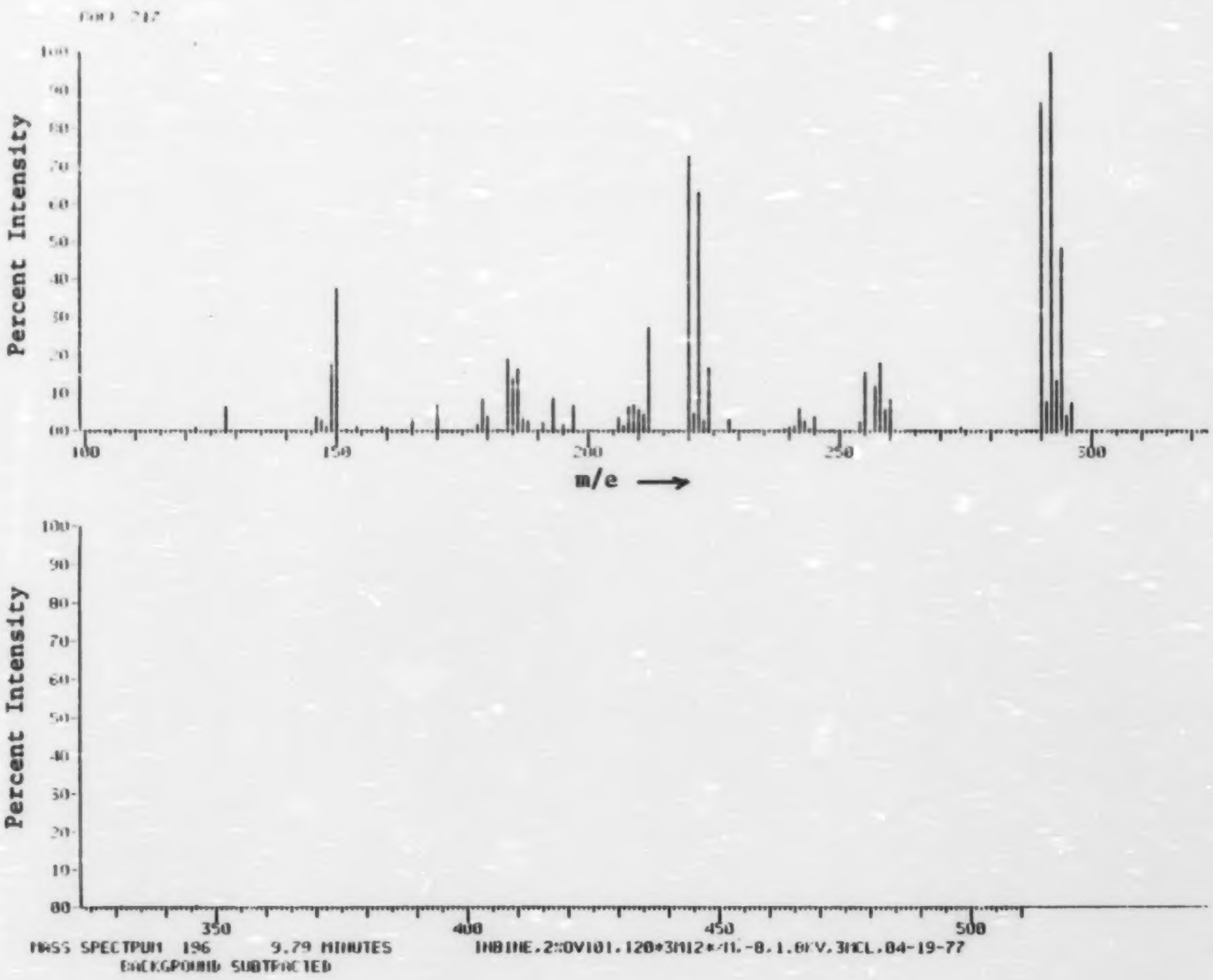


Figure C-5. Mass spectrum of tetrachlorobiphenyl (M = 290) identified in neutral extract of New Bedford sludge.

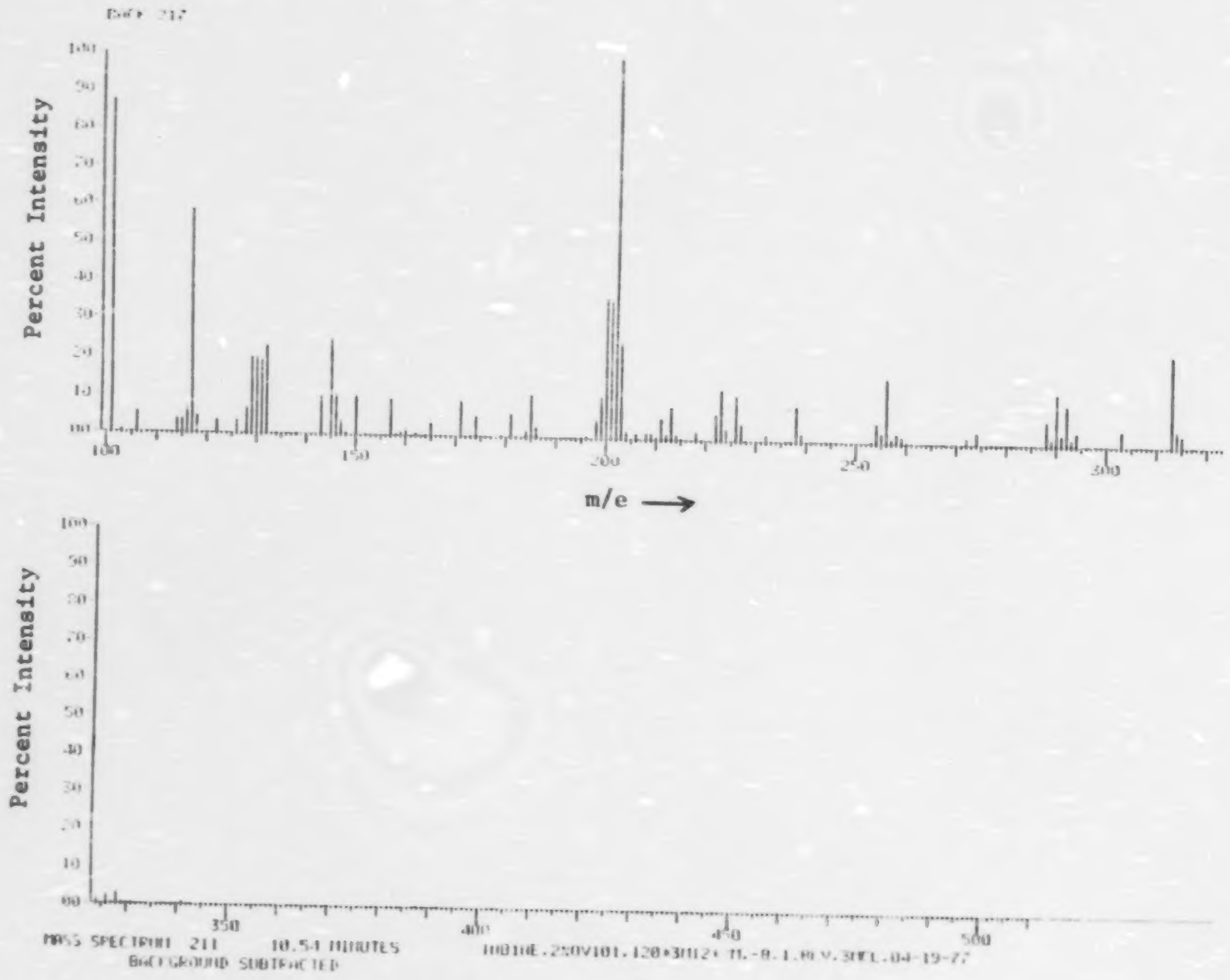


Figure C-6. Mass spectrum of pentachlorobiphenyl (M = 324) identified in neutral extract of New Bedford sludge.

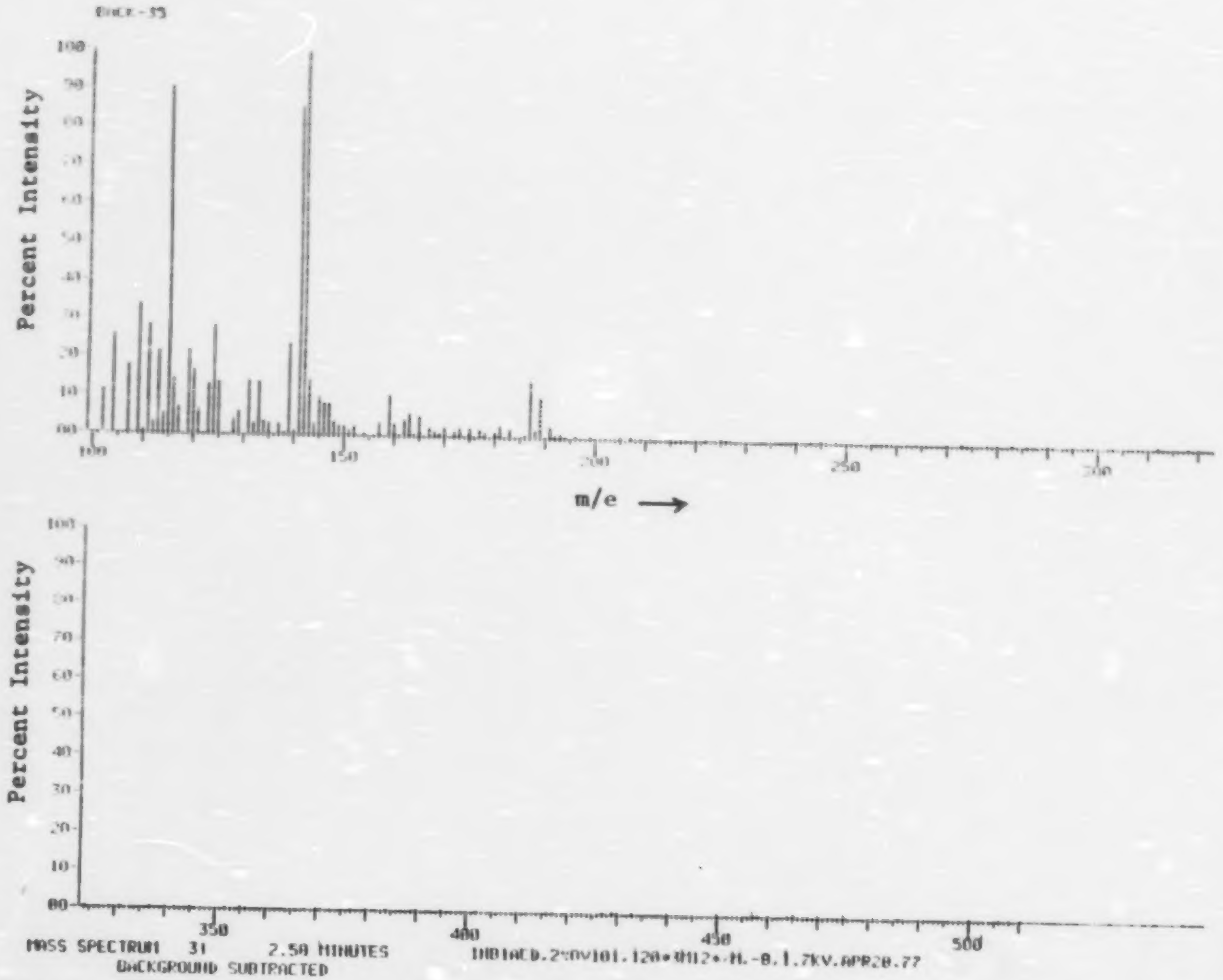


Figure C-7. Mass spectrum of unknown dichloro-compound (M = 187) found in diazomethane-methylated extract of New Bedford sludge.

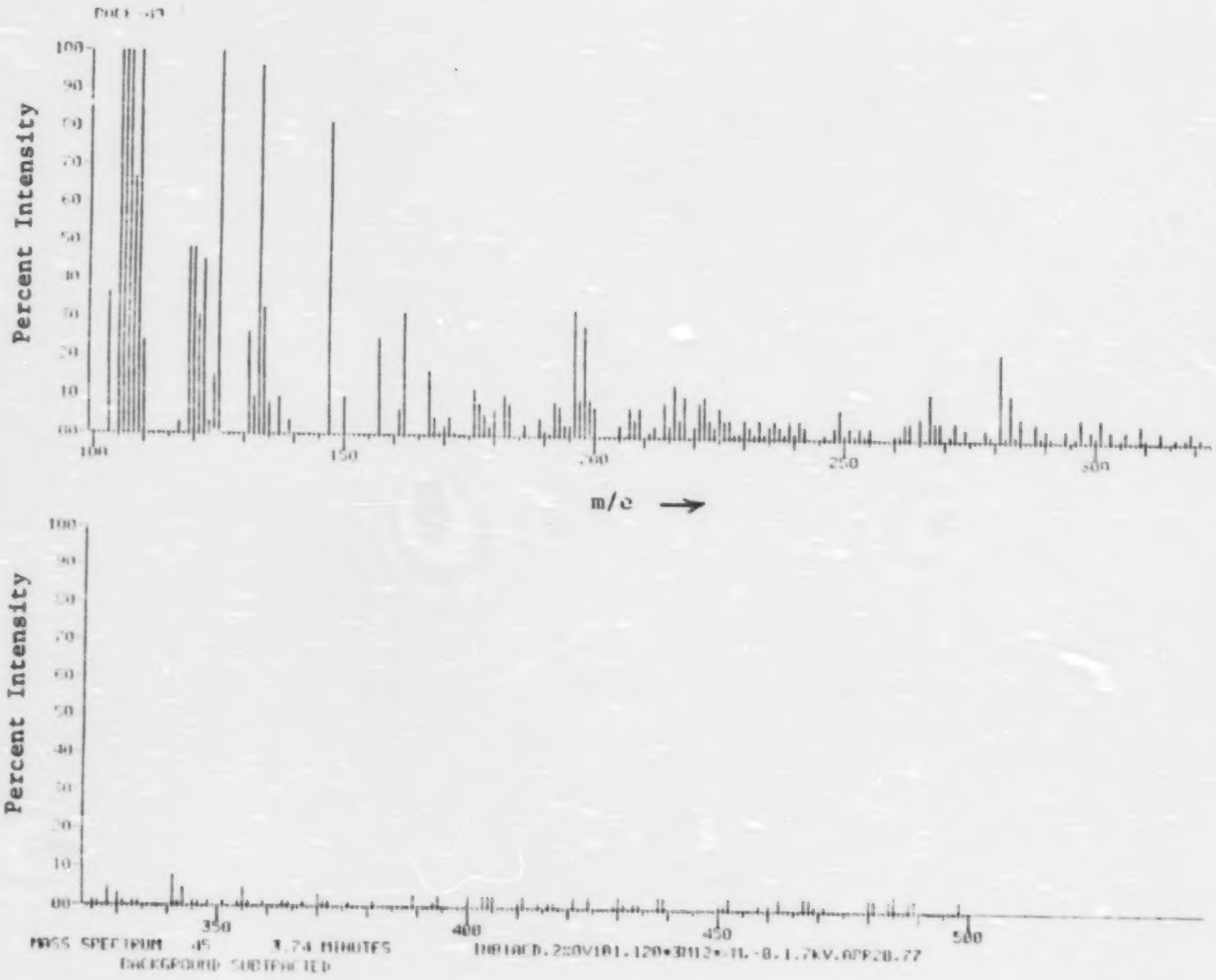


Figure C-8. Mass spectrum of dichloronaphthalene (M = 196) tentatively identified in diazomethane-methylated extract of New Bedford sludge.

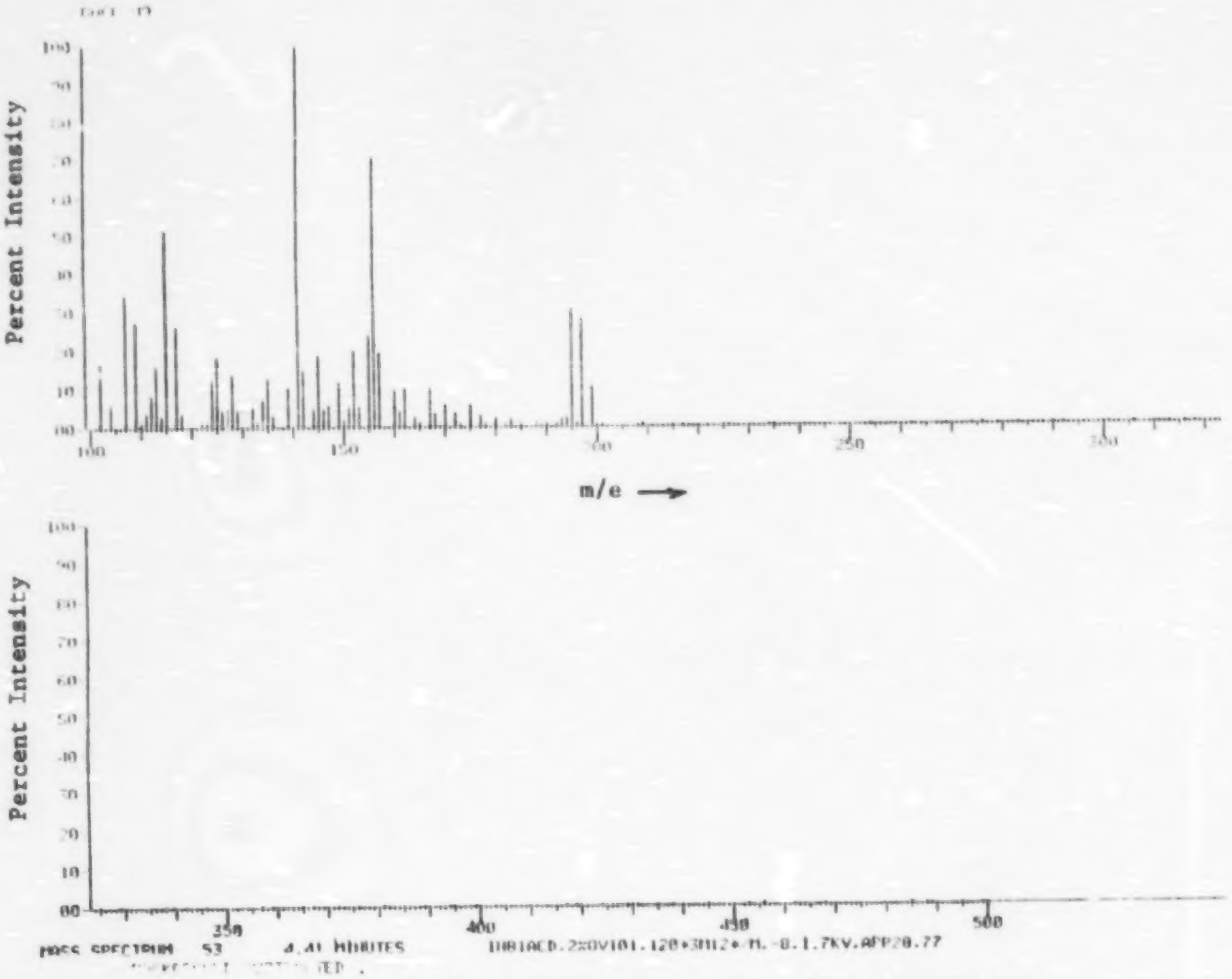


Figure C-9. Mass spectrum of trichloroaniline (M = 195) identified in diazomethane-methylated extract of New Bedford sludge.

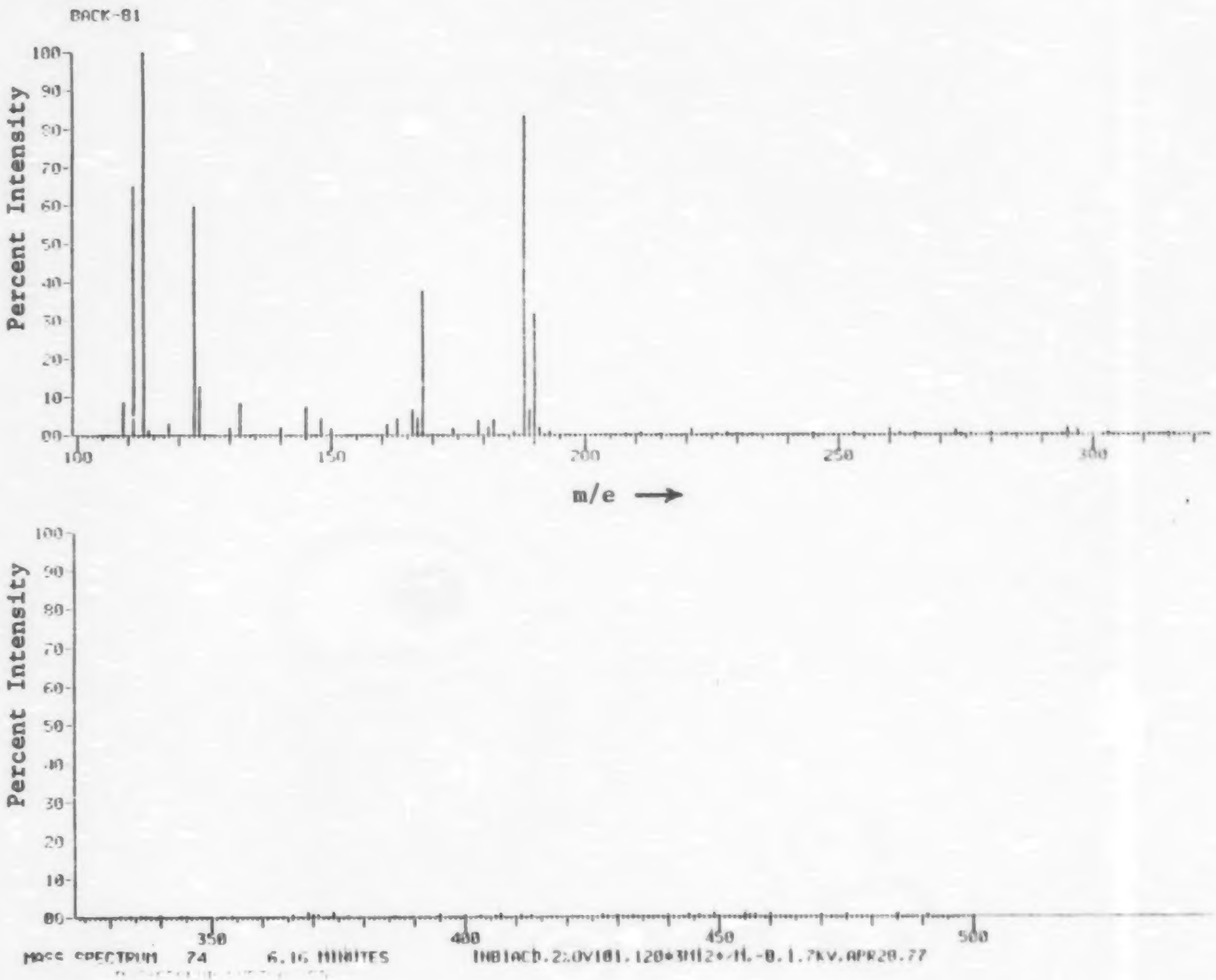


Figure C-10. Mass spectrum of chlorobiphenyl (M = 188) identified in diazomethane-methylated extract of New Bedford sludge.

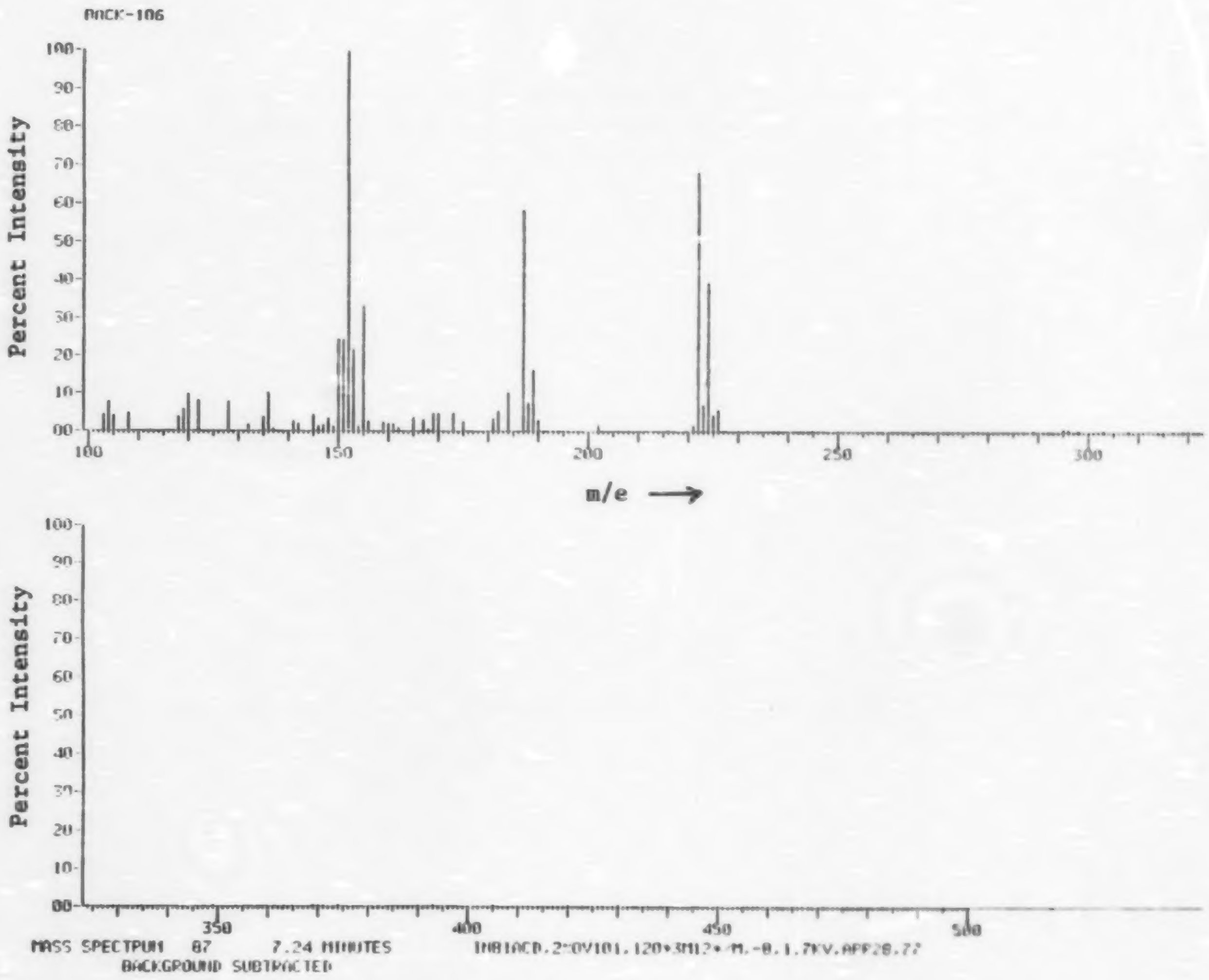


Figure C-11. Mass spectrum of dichlorobiphenyl (M = 222) identified in diazomethane-methylated extract of New Bedford sludge.

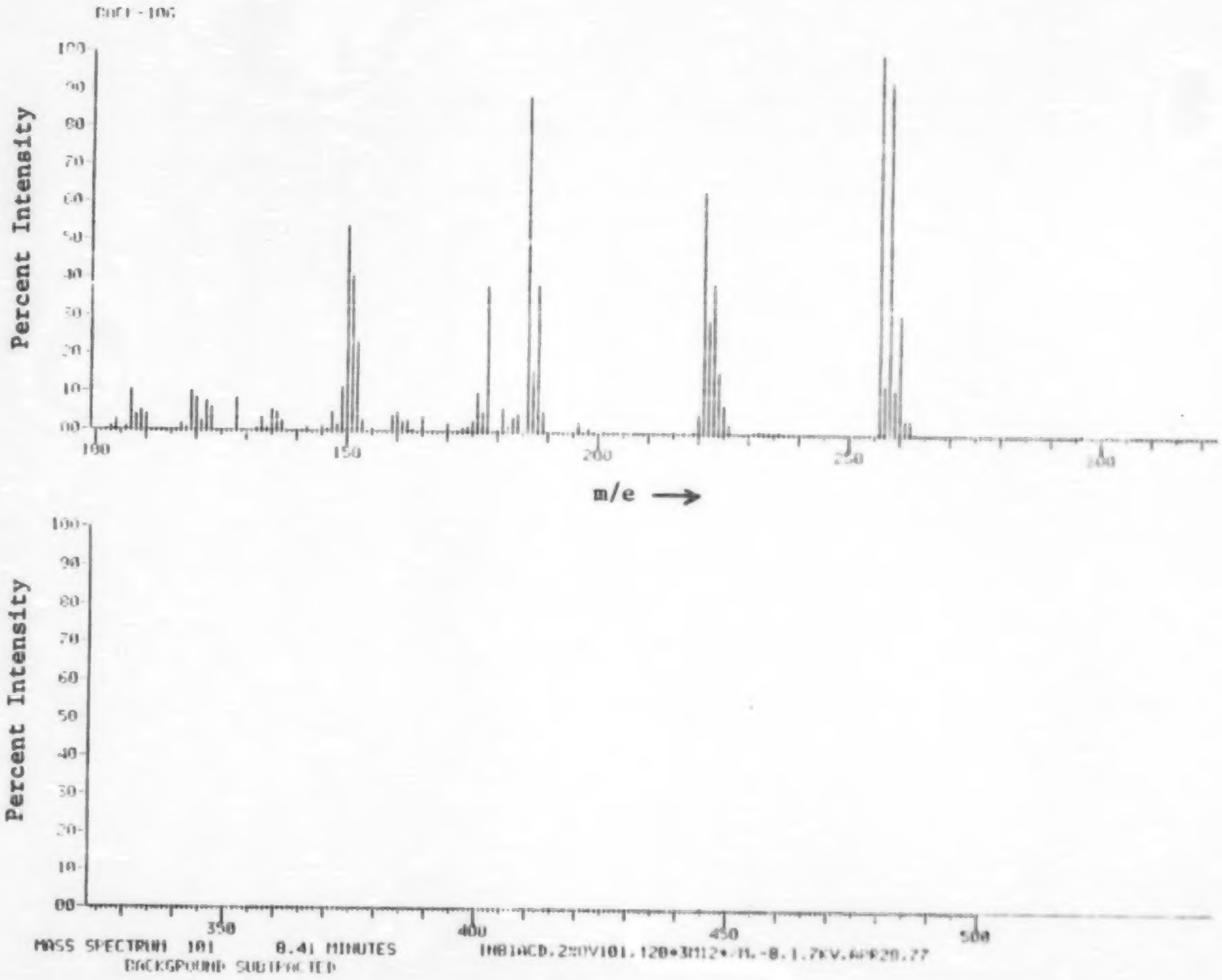


Figure C-12. Mass spectrum of trichlorobiphenyl (M = 256) identified in diazomethane-methylated extract of New Bedford sludge.

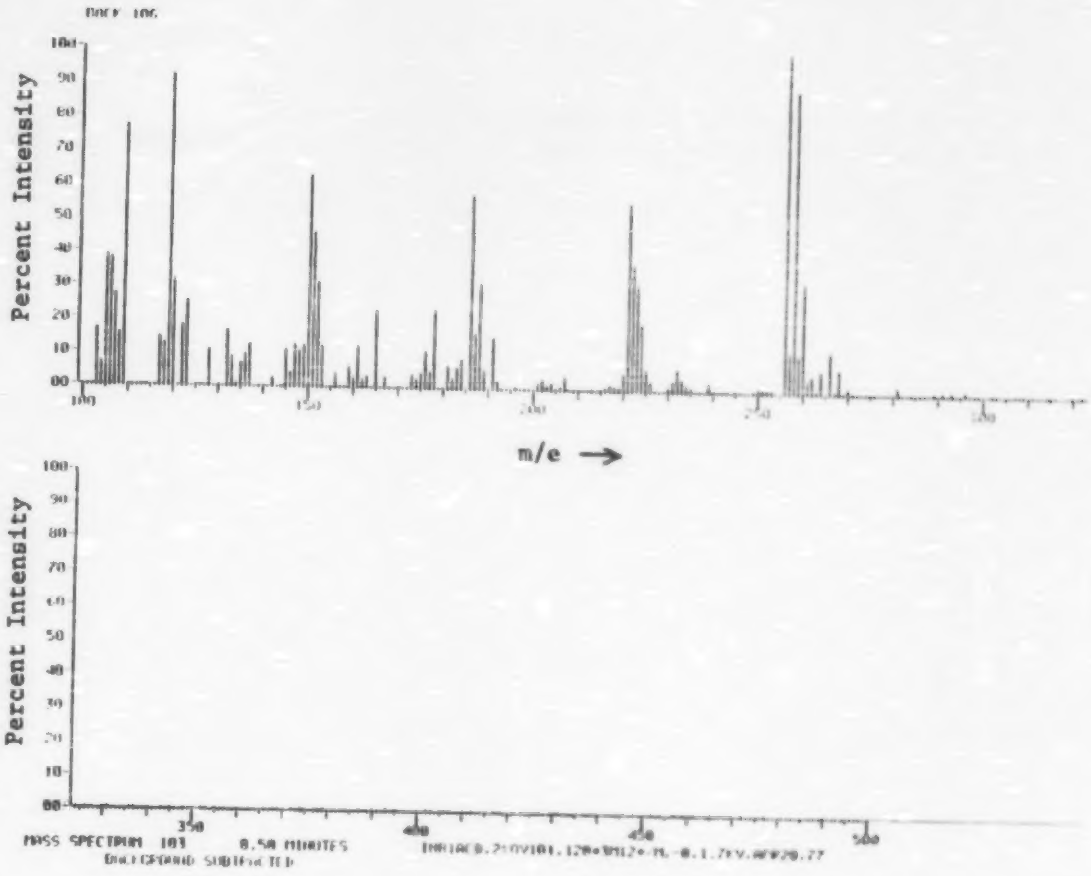


Figure C-13. Mass spectrum of trichlorobiphenyl (M = 256) and tetrachloronaphthalene (M = 264) identified in diazomethane-methylated extract of New Bedford sludge.

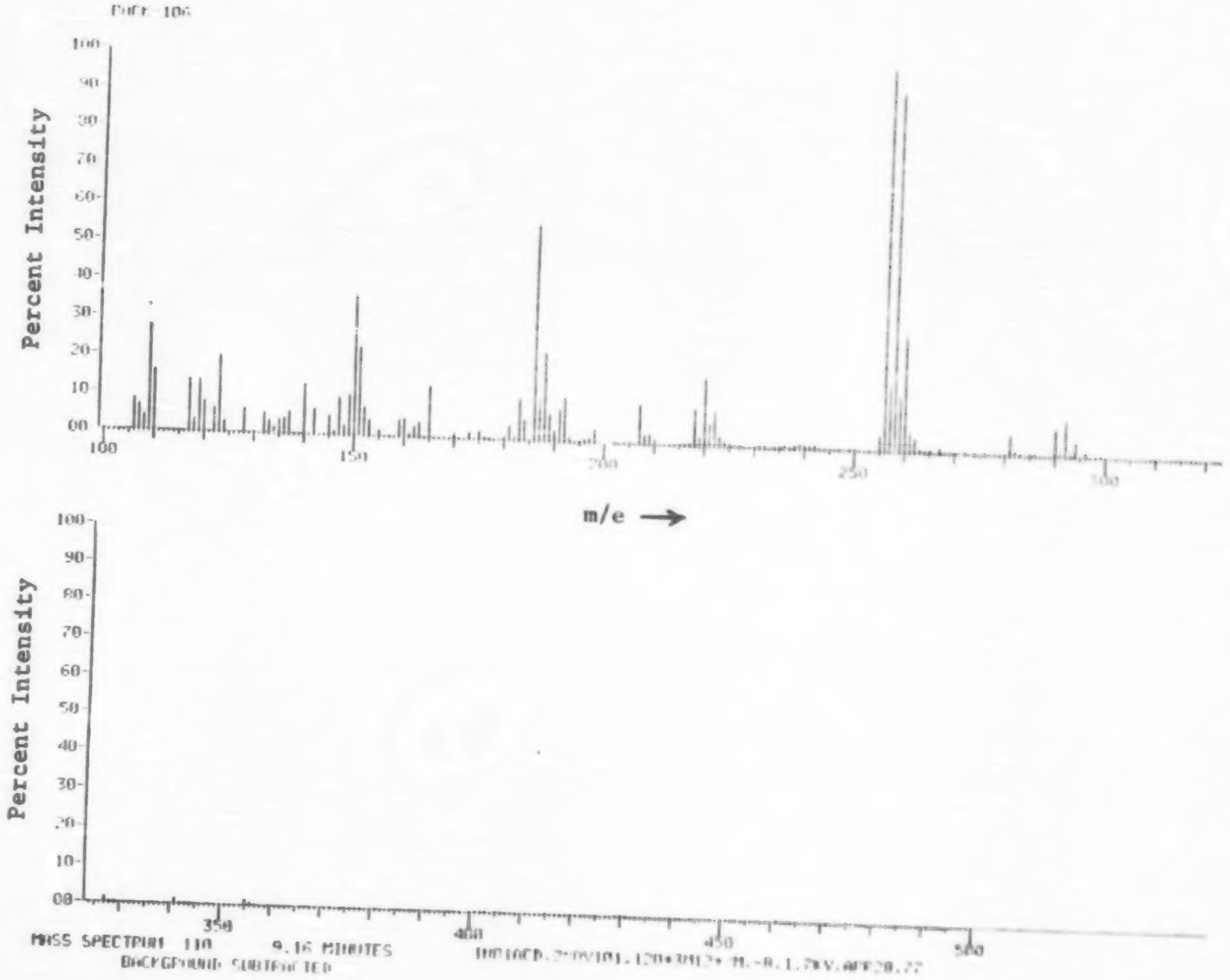


Figure C-14. Mass spectrum of tetrachlorobiphenyl (M = 290) identified in diazomethane-methylated extract of New Bedford sludge.

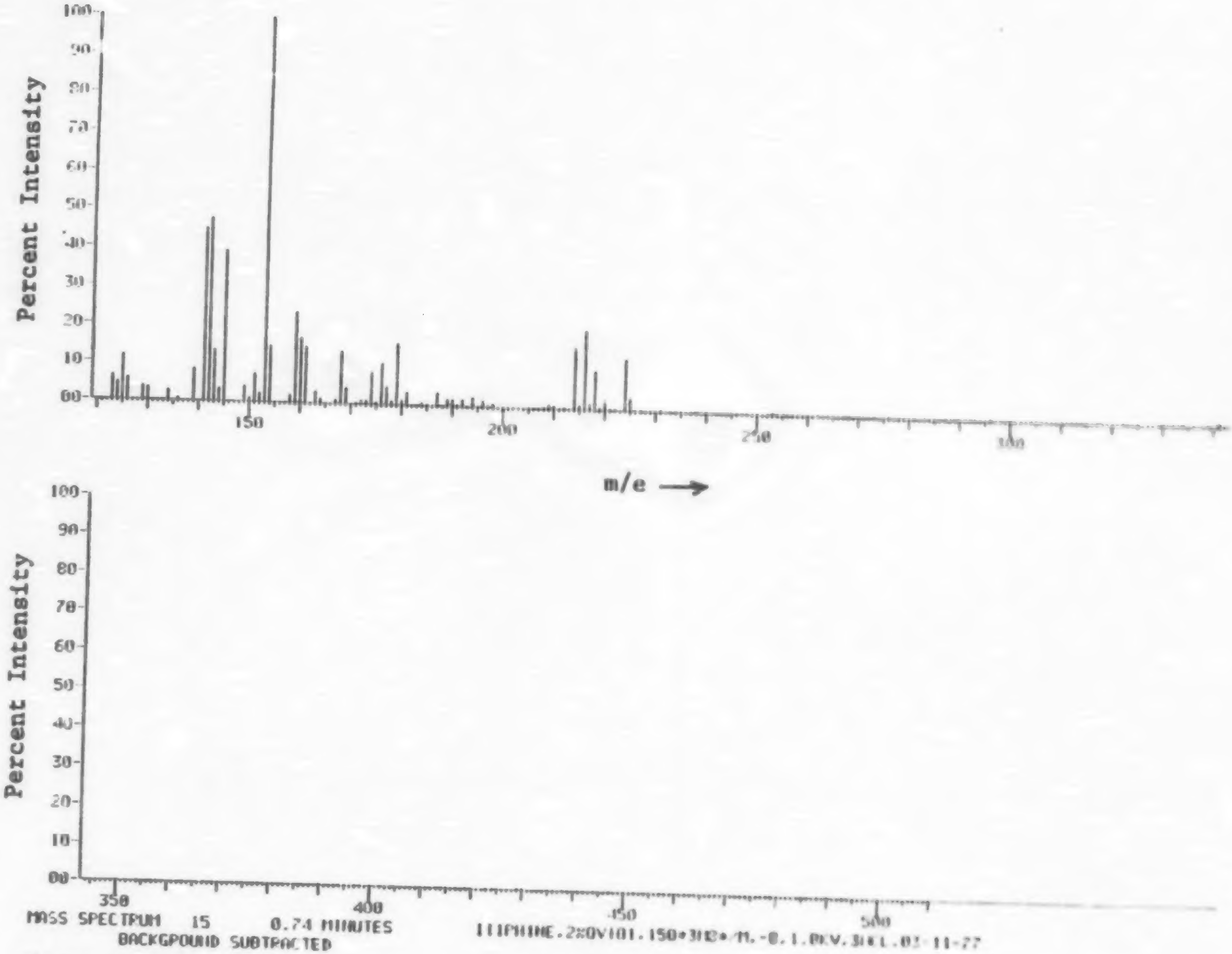


Figure C-15. Mass spectrum of tetrachlorobenzene (M = 214) identified in neutral extract of Philadelphia sludge.

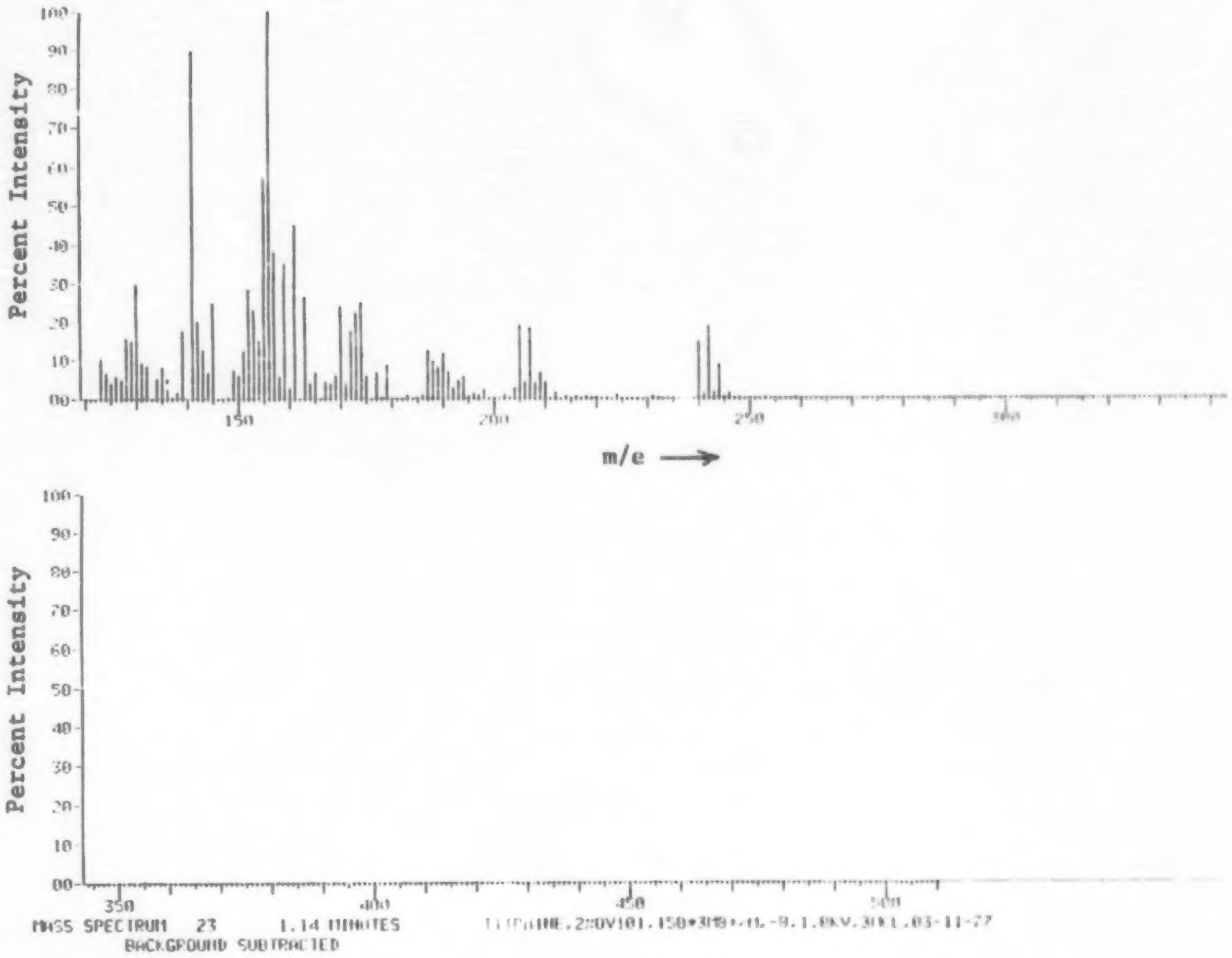


Figure C-16. Mass spectrum of tetrachloro-compound (M = 240) found in neutral extract of Philadelphia sludge.

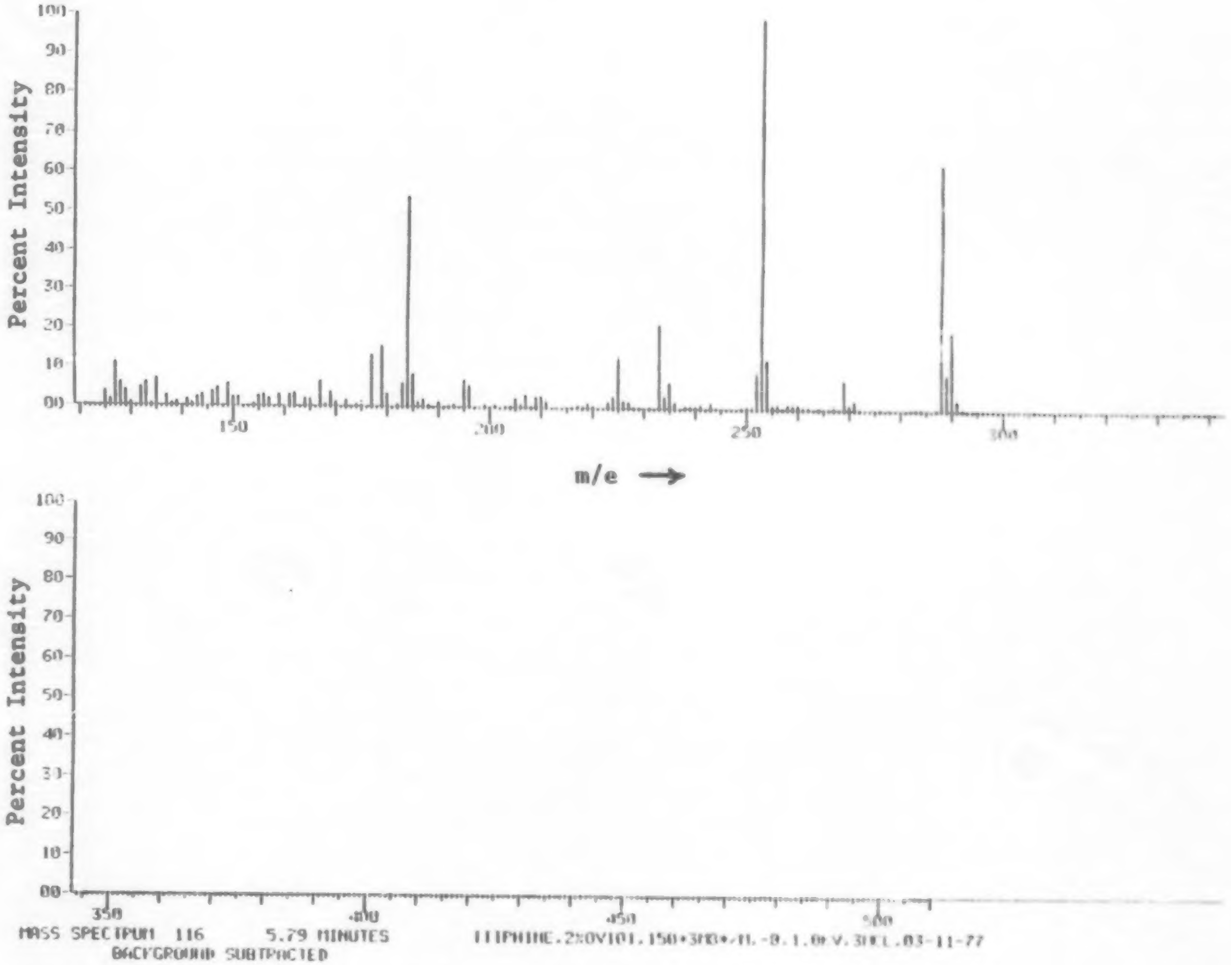


Figure C-17. Mass spectrum of monochloro-compound (M = 288) found in neutral extract of Philadelphia sludge.

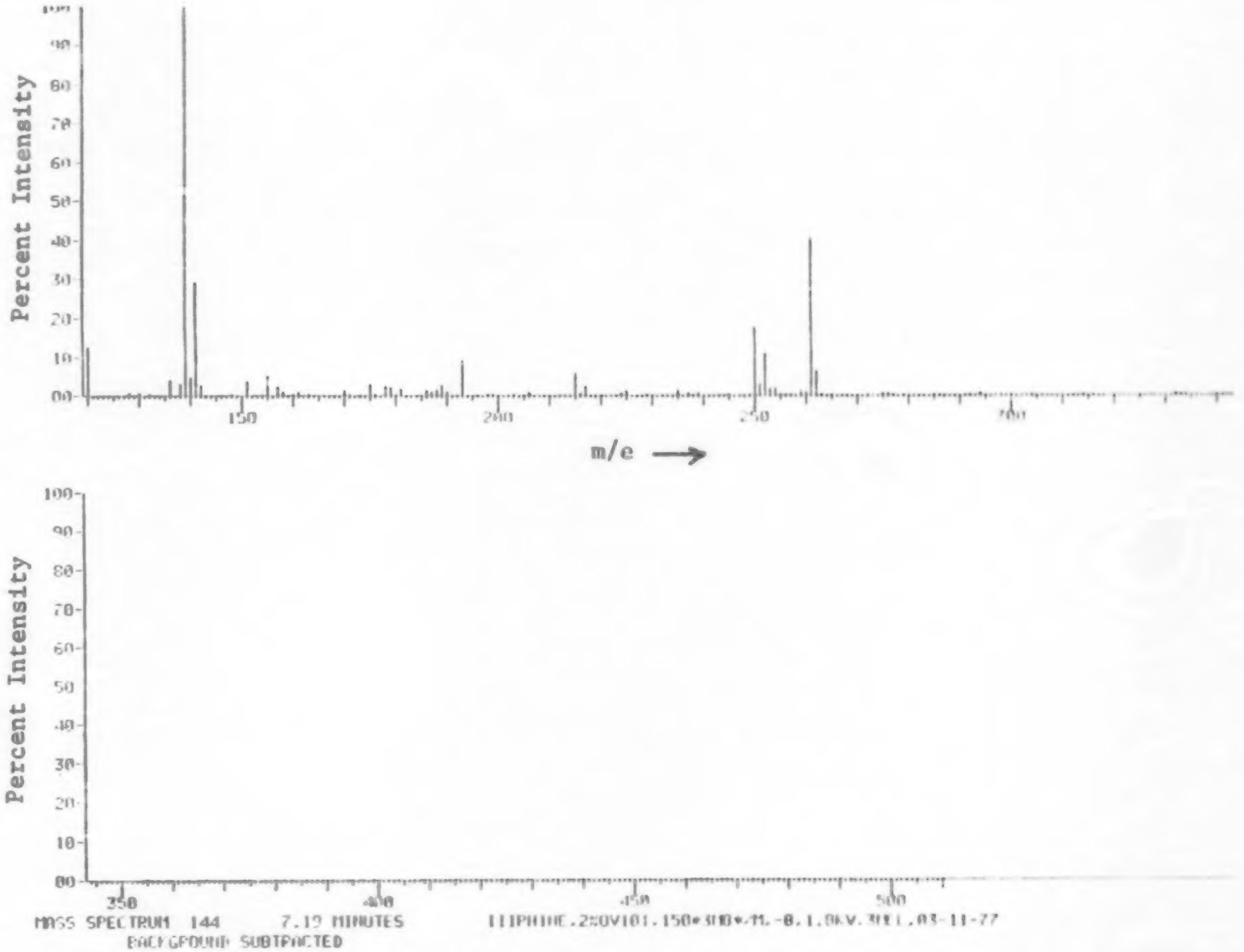


Figure C-18. Mass spectrum of dichlorobenzophenone (M = 250) identified in neutral extract of Philadelphia sludge.

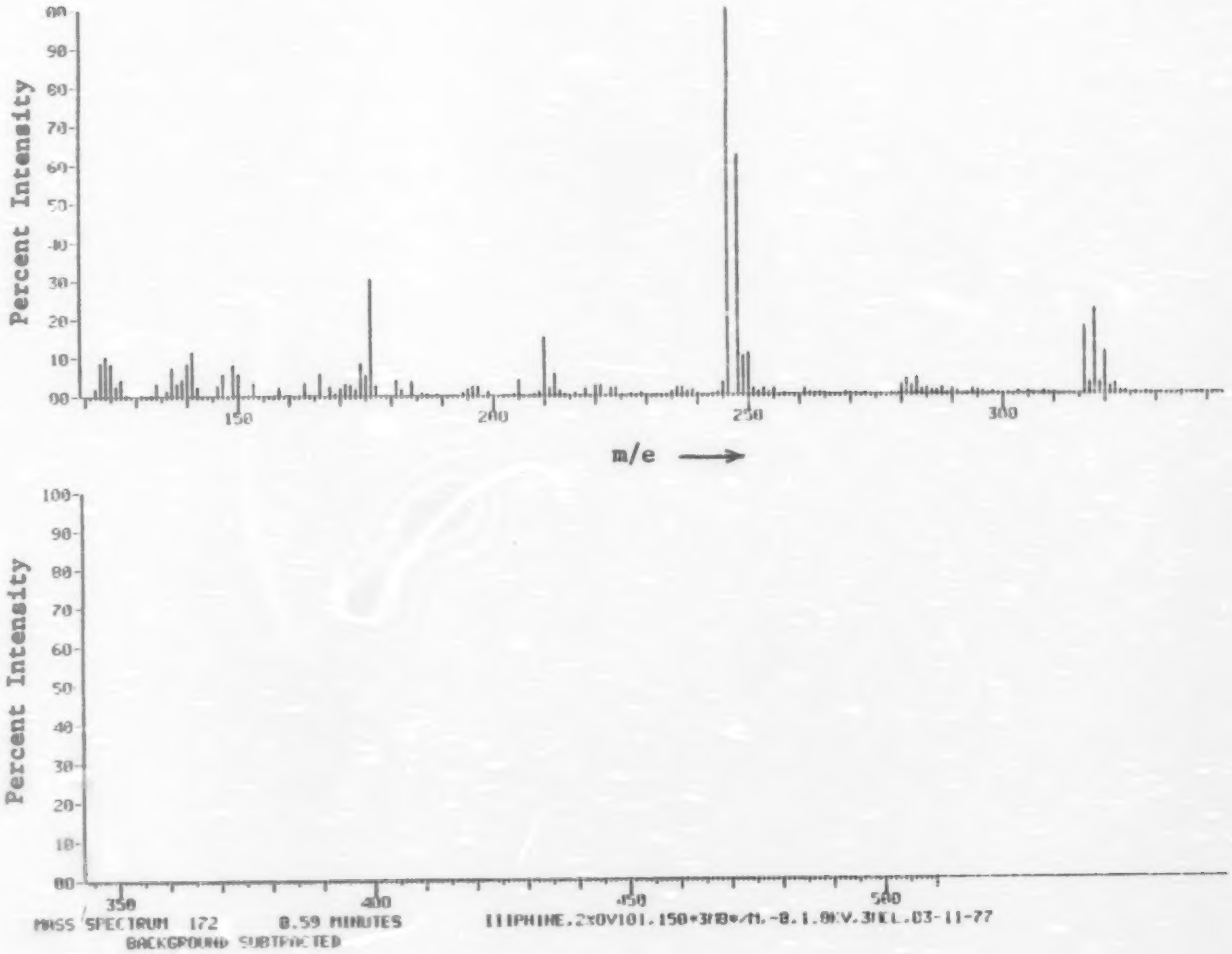


Figure C-19. Mass spectrum of DDE (M = 316) identified in neutral extract of Philadelphia sludge.

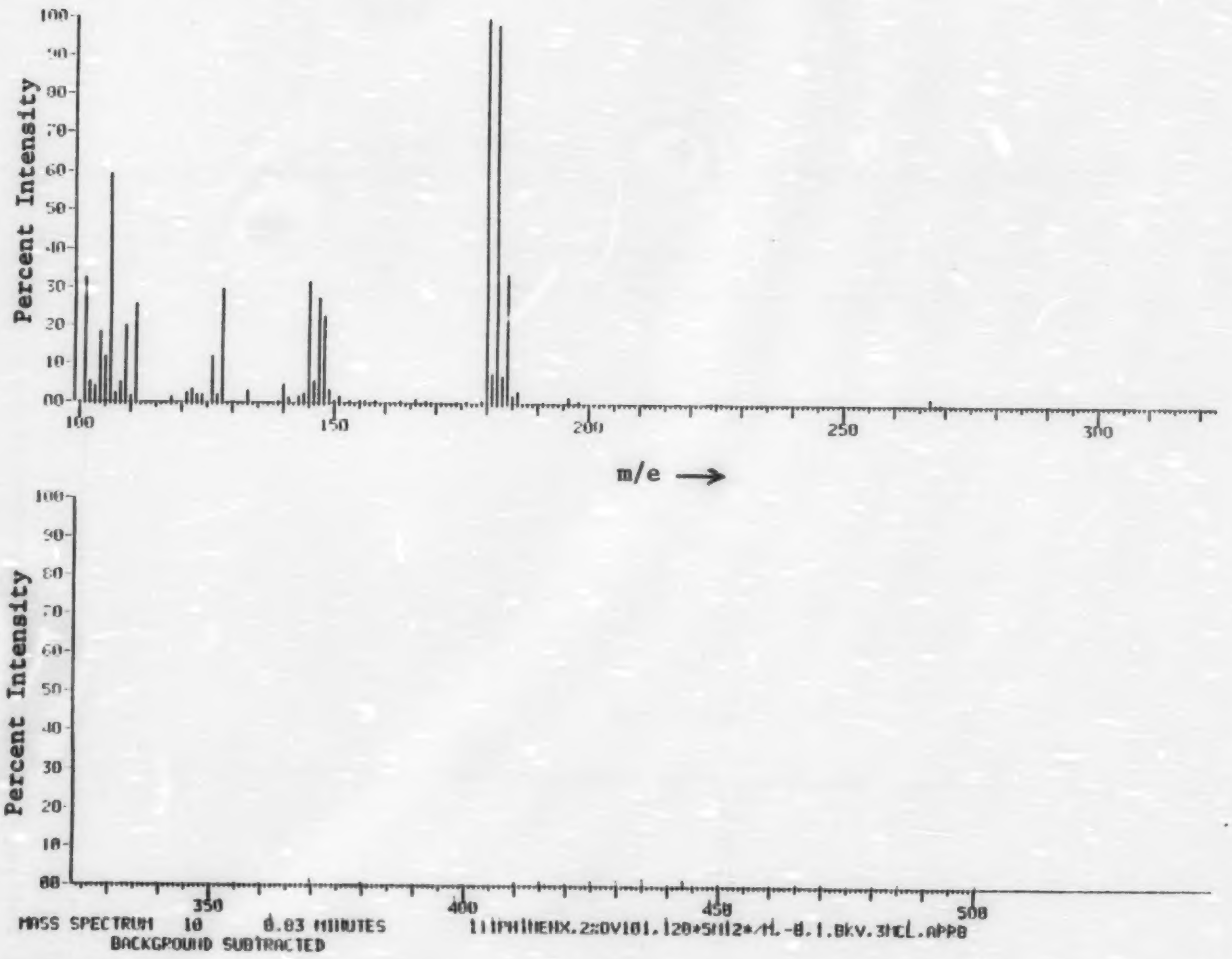


Figure C-20. Mass spectrum of trichlorobenzene (M = 180) identified in hexane eluate of neutral extract of Philadelphia sludge.

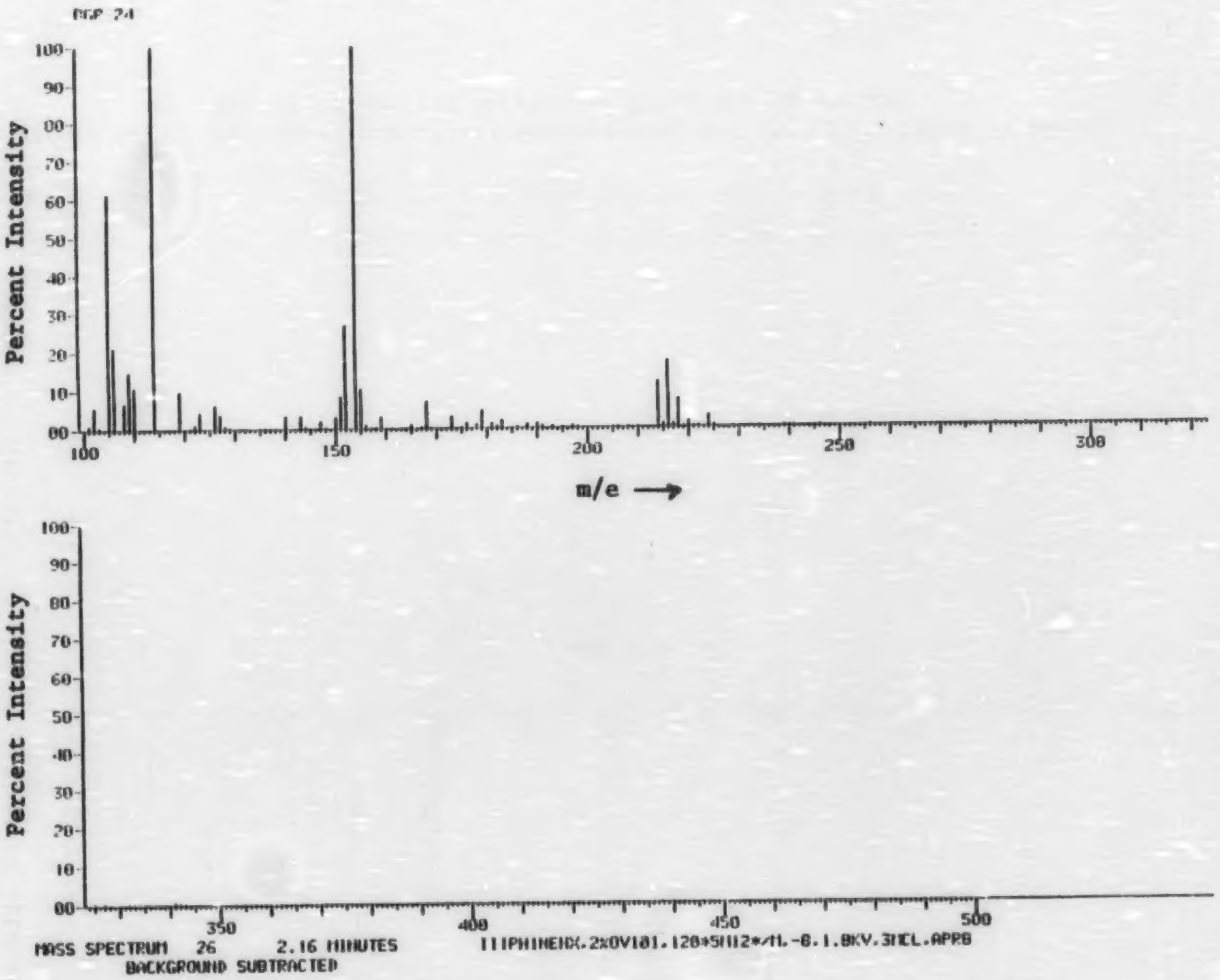


Figure C-21. Mass spectrum of tetrachlorobenzene (M = 214) identified in neutral extract of Philadelphia sludge.

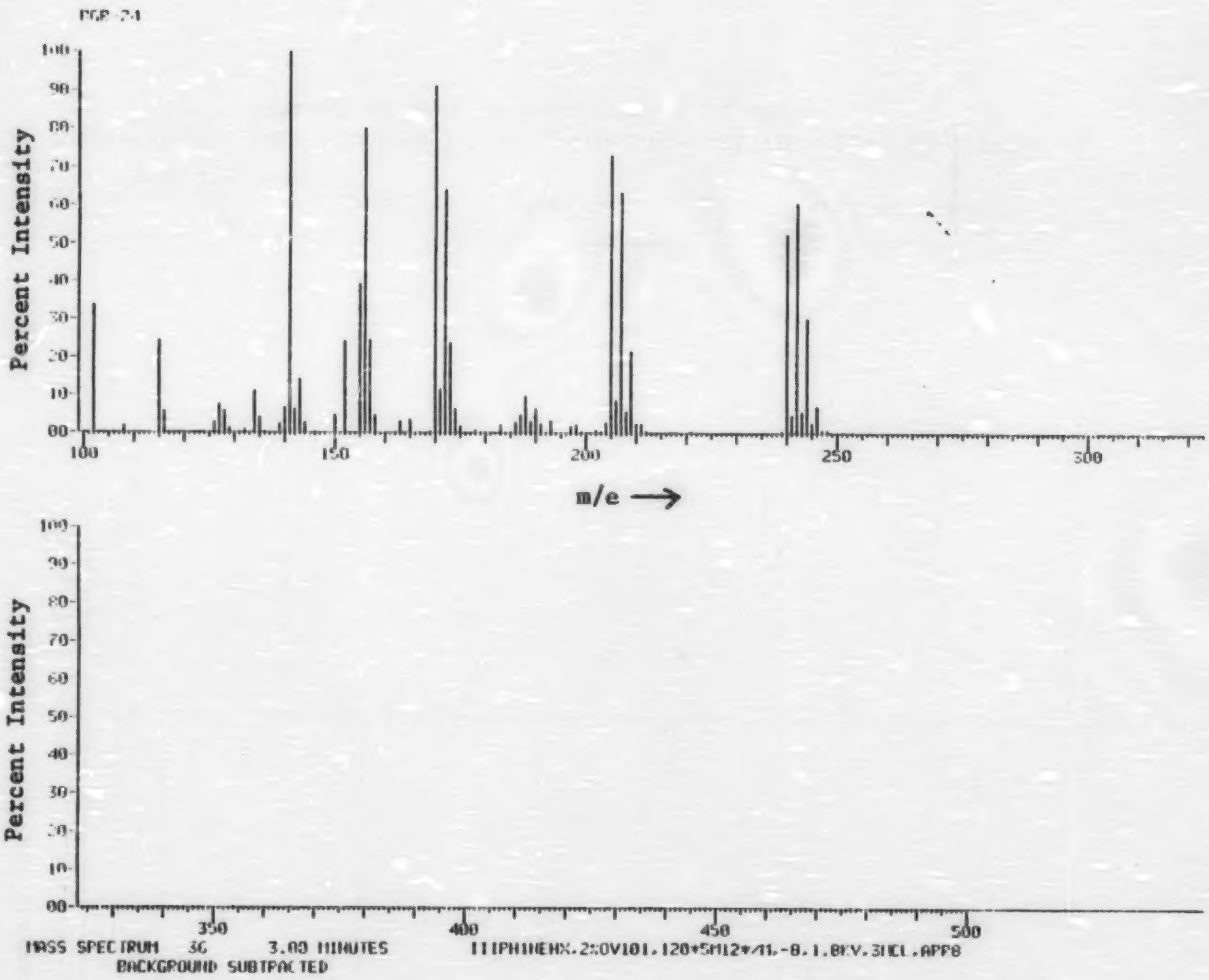


Figure C-22. Mass spectrum of tetrachloro-compound (M = 240) found in hexane eluate of neutral extract of Philadelphia sludge.

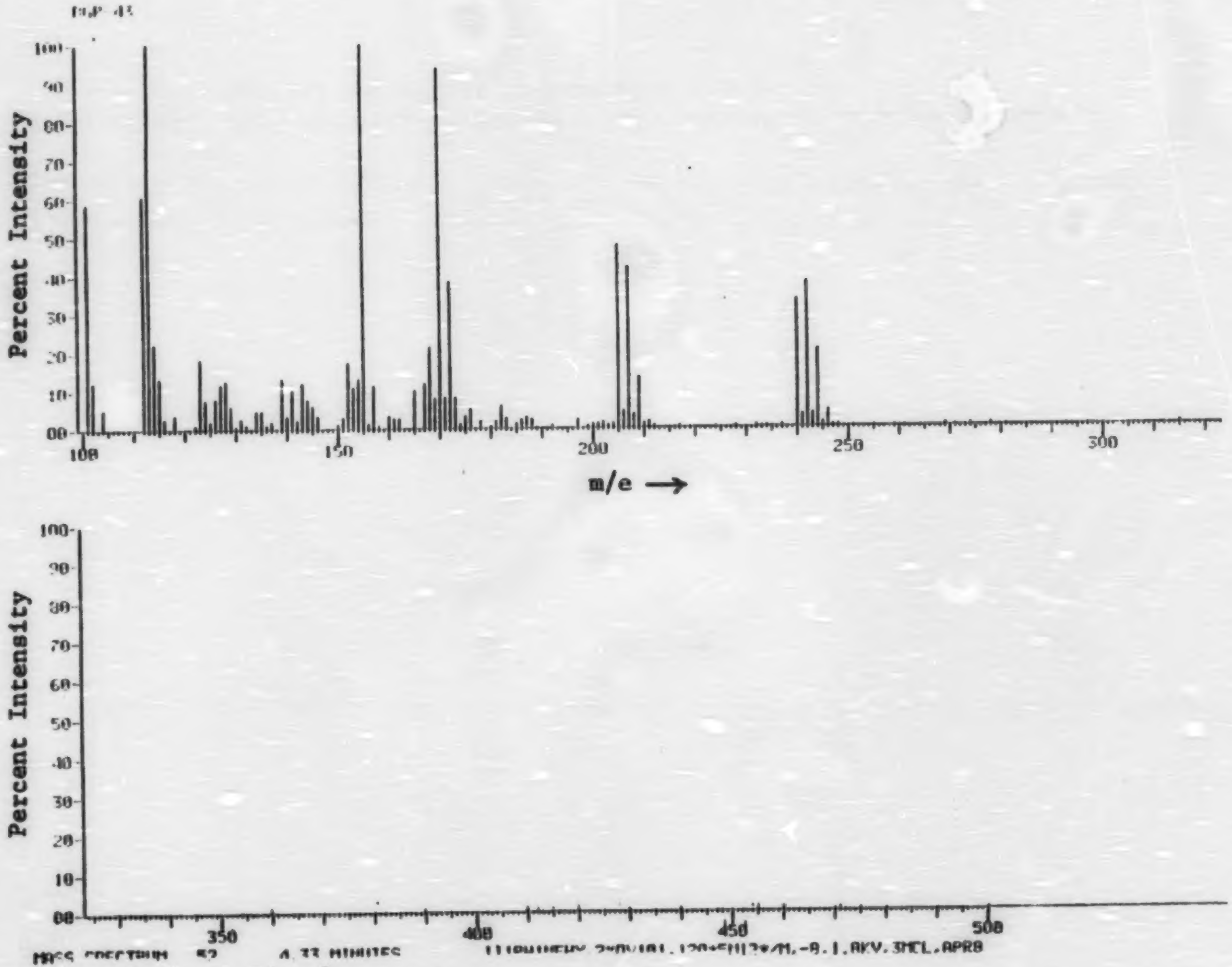


Figure C-23. Mass spectrum of tetrachloro-compound (M = 240) identified in hexane eluate of neutral extract of Philadelphia sludge.

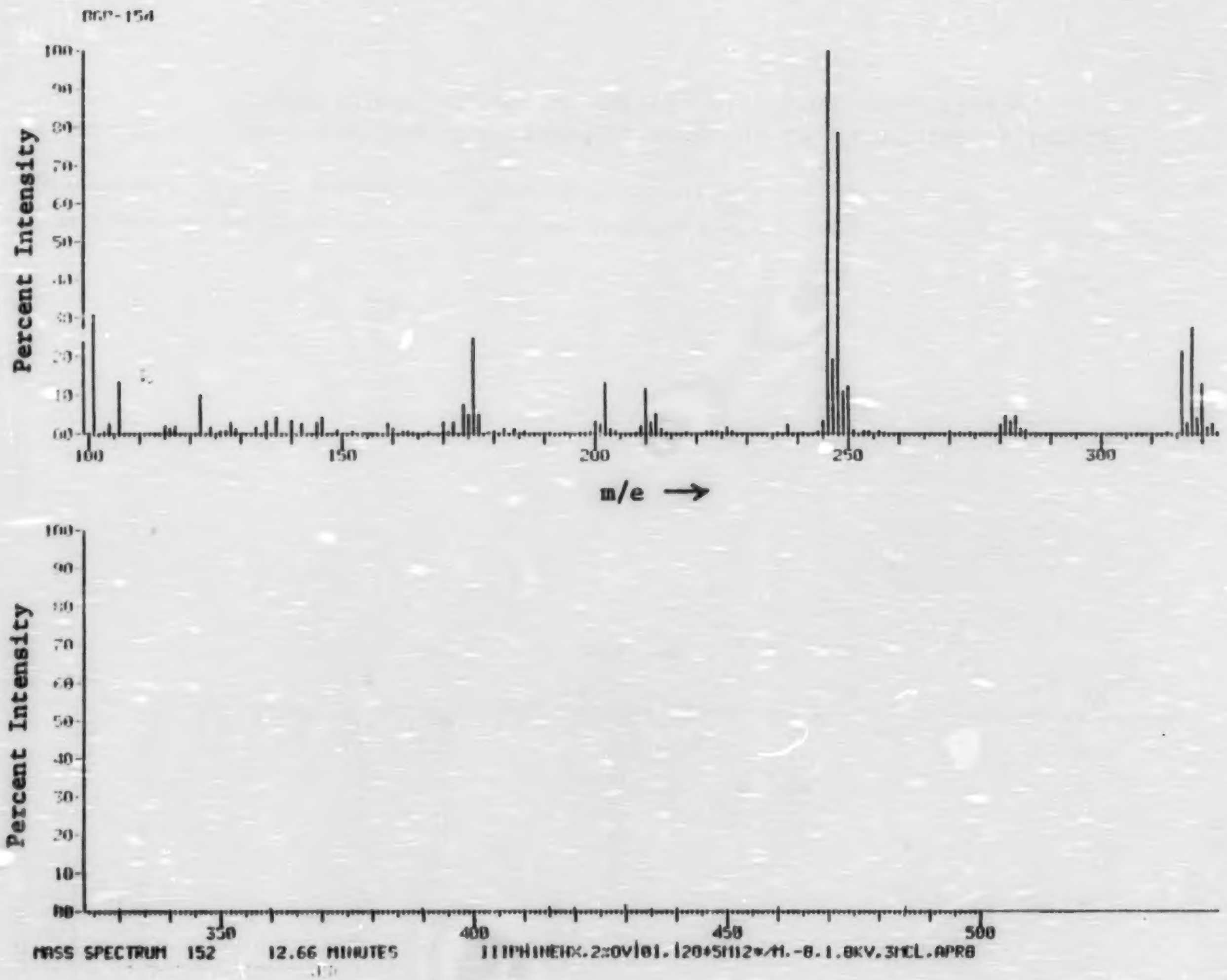


Figure C-24. Mass spectrum of DDE (M = 316) identified in hexane eluate of neutral extract of Philadelphia sludge.

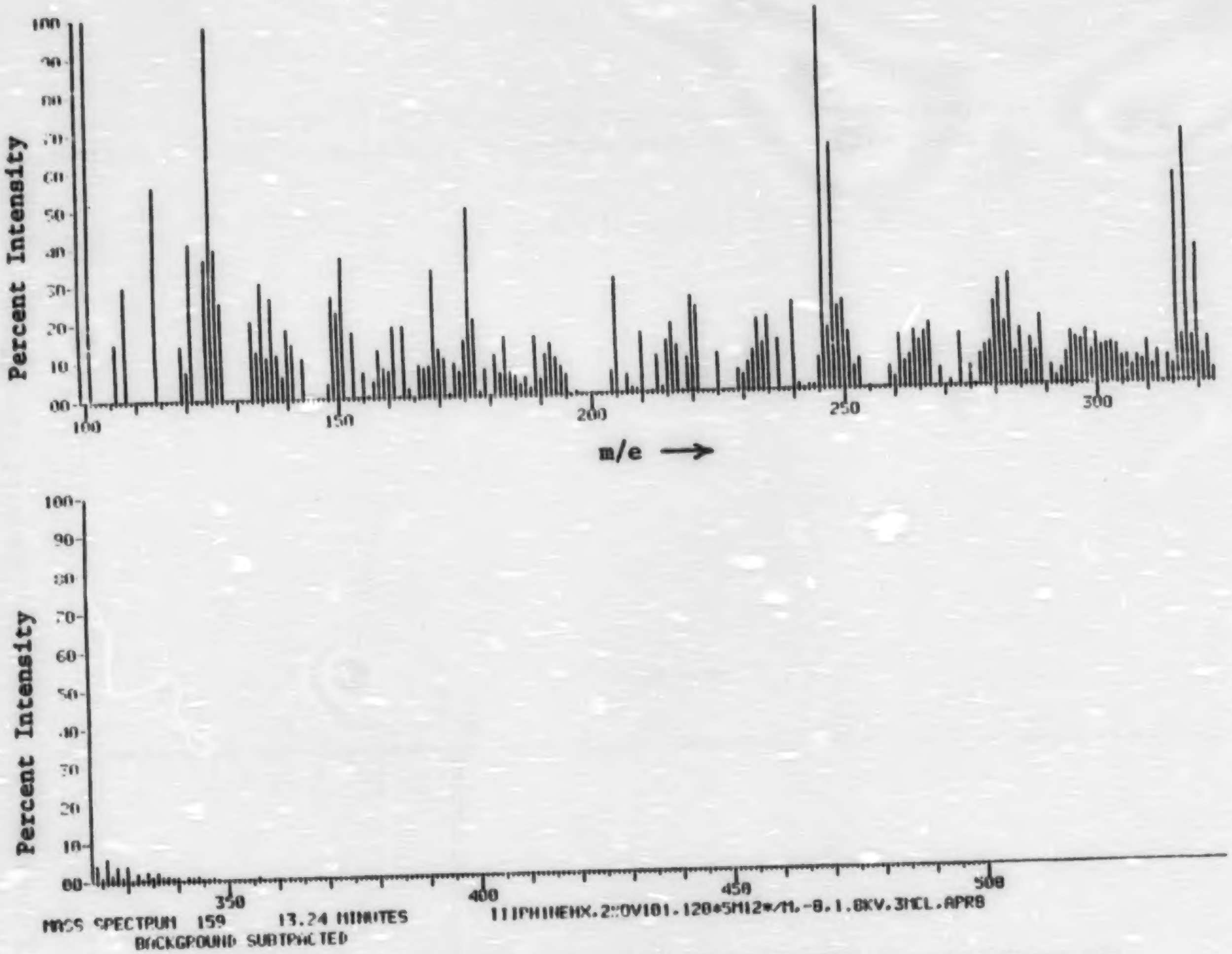


Figure C-25. Mass spectrum of DDE (M = 316) identified in hexane eluate of neutral extract of Philadelphia sludge.

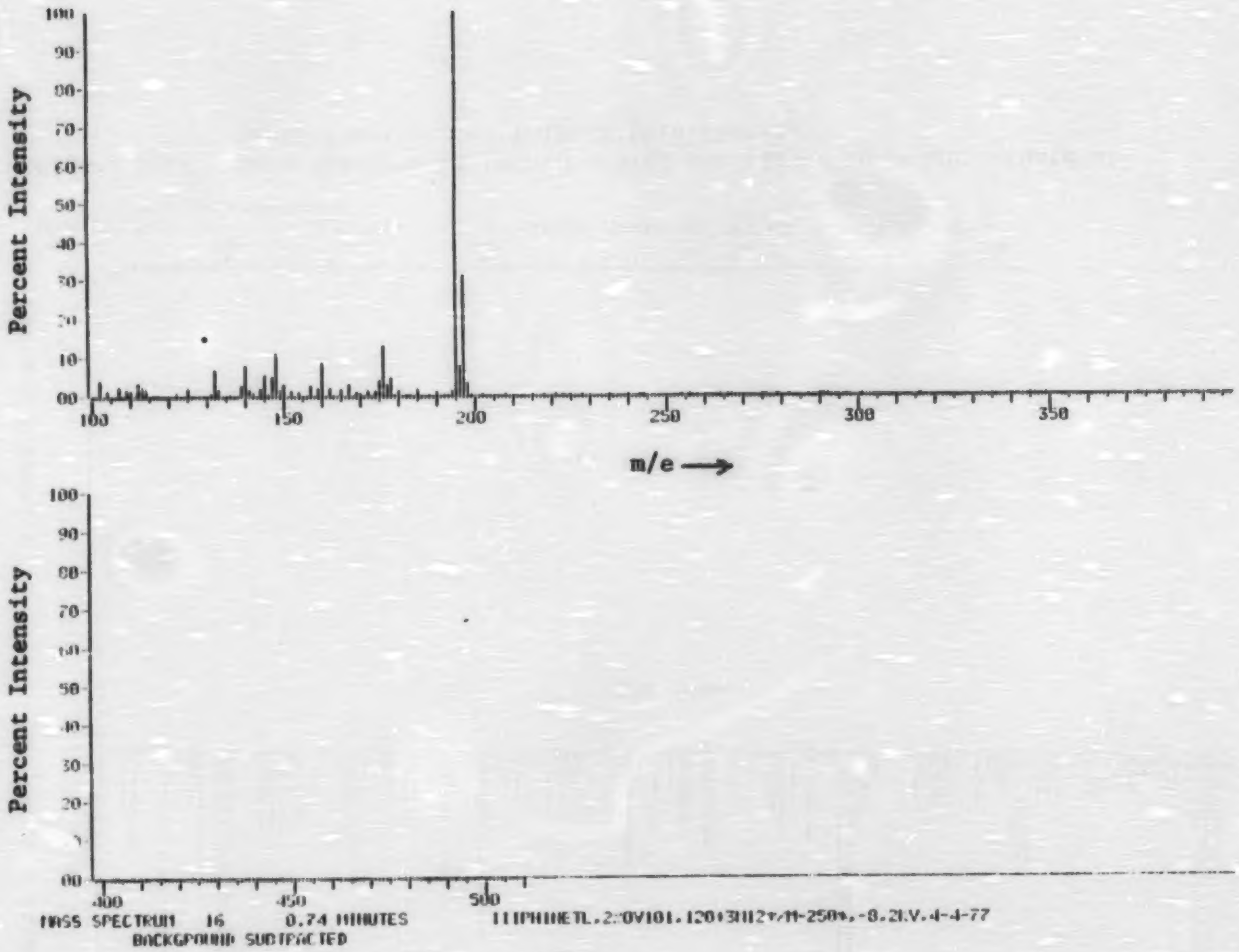


Figure C-26. Mass spectrum of monochloro-compound (M = 195) found in toluene eluate of neutral extract of Philadelphia sludge.

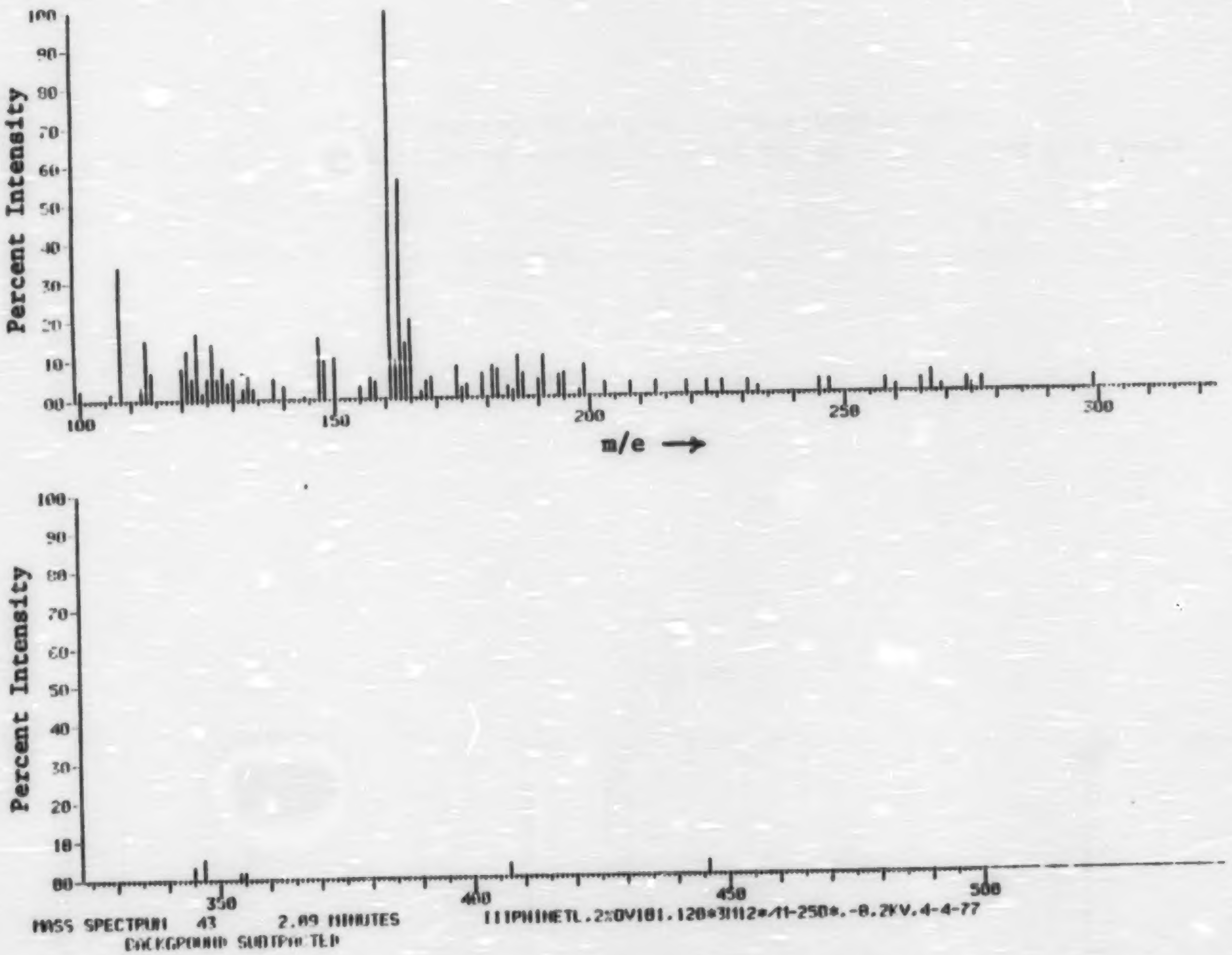


Figure C-27. Mass spectrum of dichloroaniline (M = 161) identifed in toluene eluate of neutral extract of Philadelphia sludge.

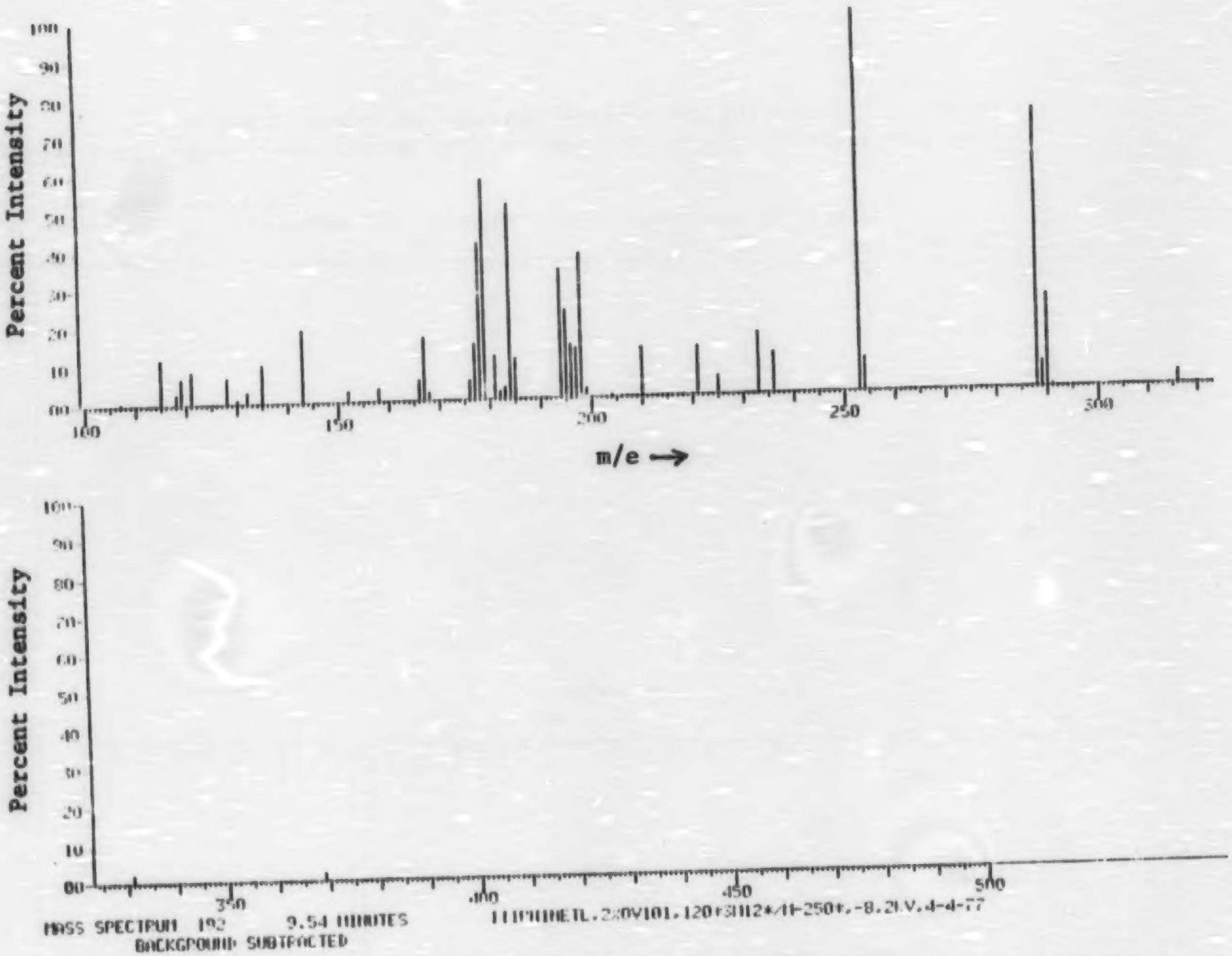


Figure C-28. Mass spectrum of monochloro-compound (M = 288) found in toluene eluate of neutral extract of Philadelphia sludge.

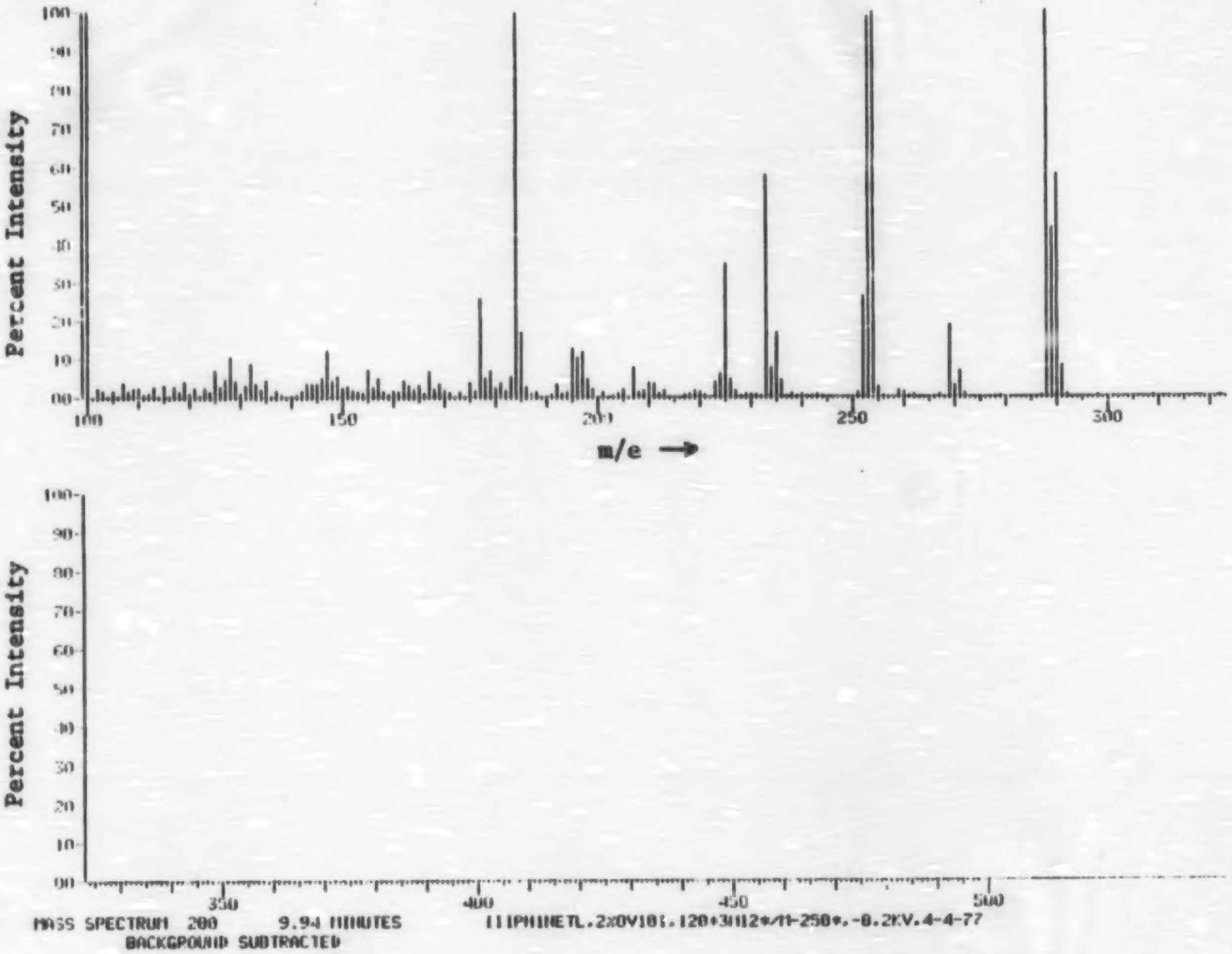


Figure C-29. Mass spectrum of monochloro-compound (M = 269) found in toluene eluate of neutral extract of Philadelphia sludge.

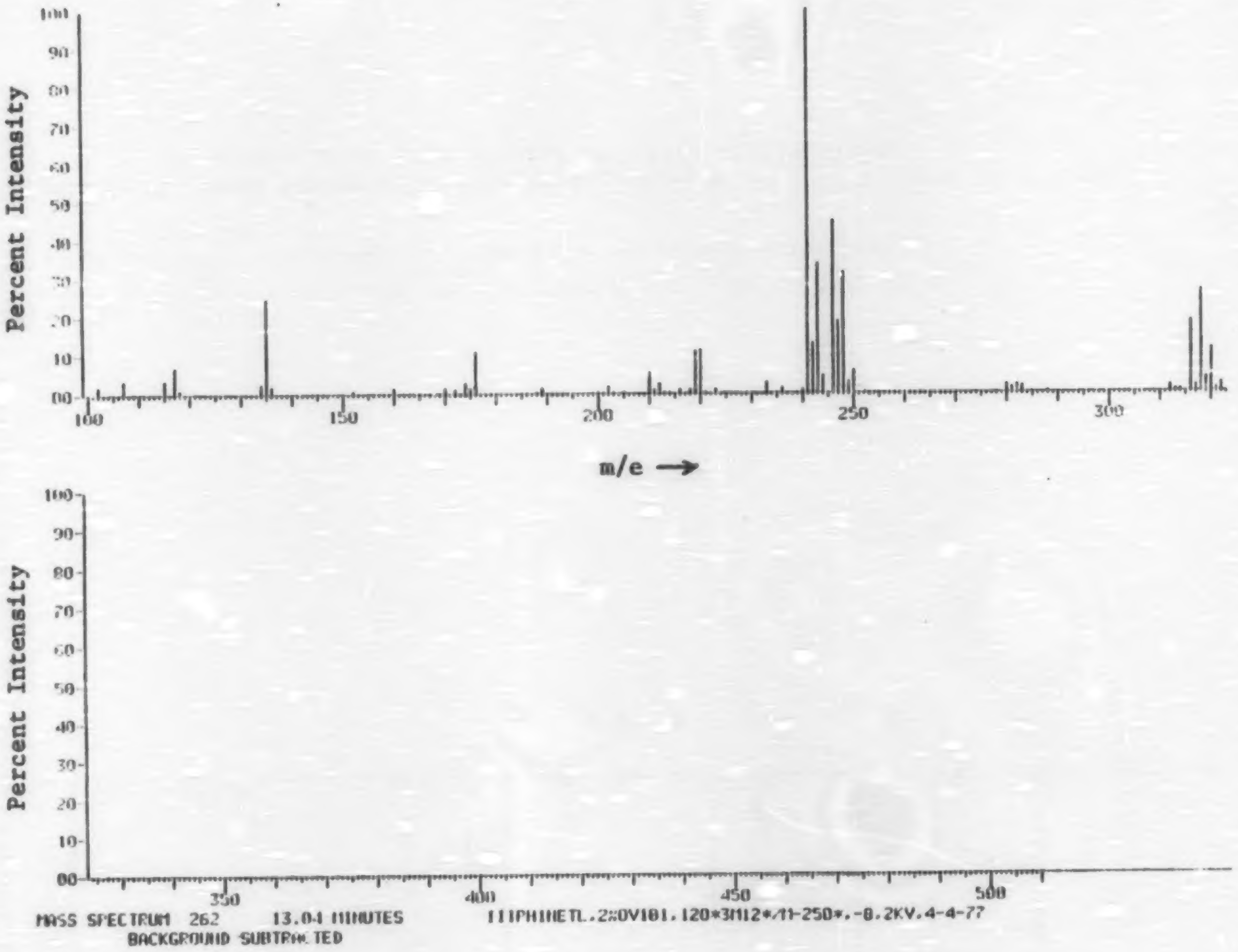


Figure C-30. Mass spectrum of DDE (M = 316) identified in toluene eluate of neutral extract of Philadelphia sludge.

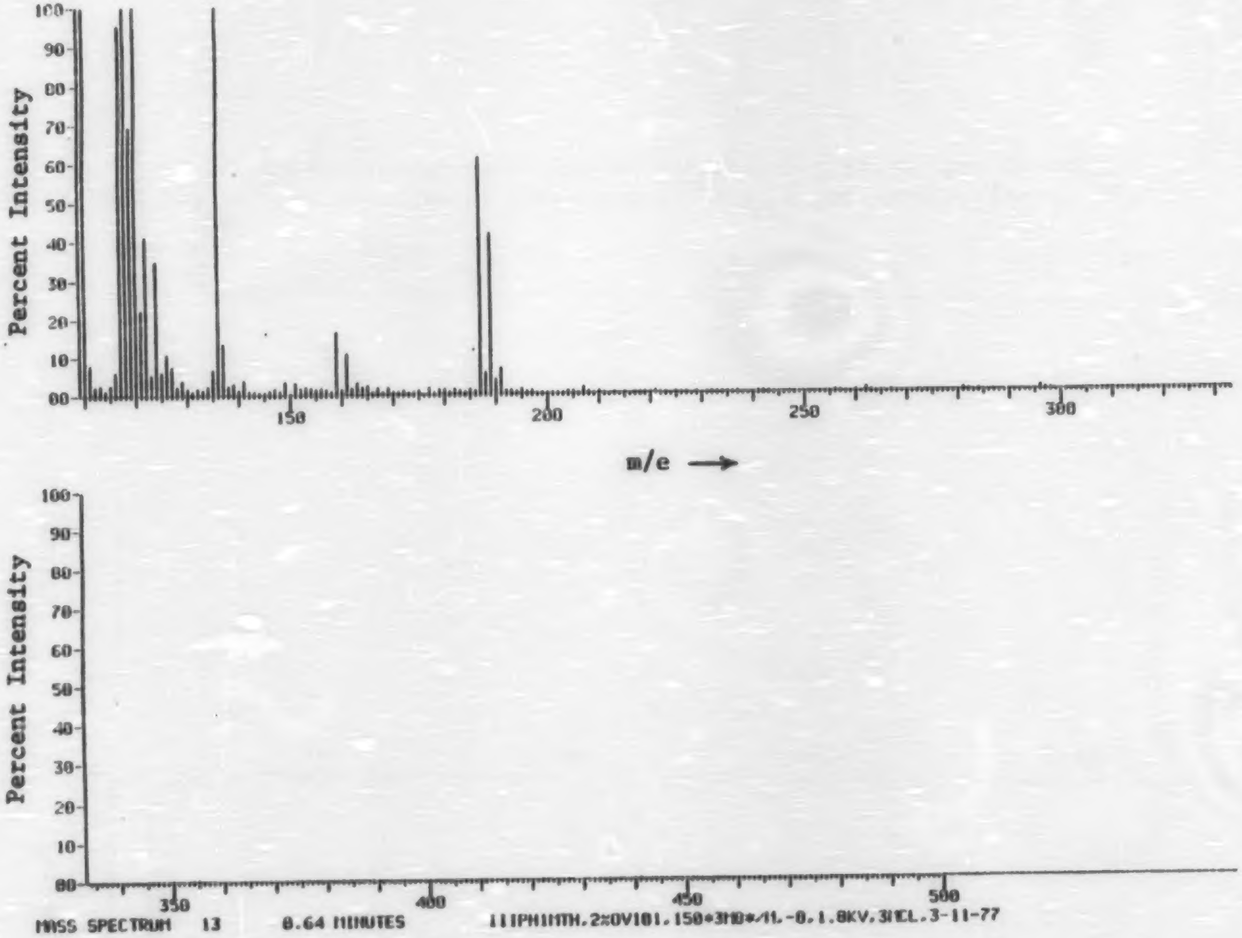


Figure C-31. Mass spectrum of dichloro-compound (M = 187) found in dimethylsulfate-methylated extract of Philadelphia sludge.

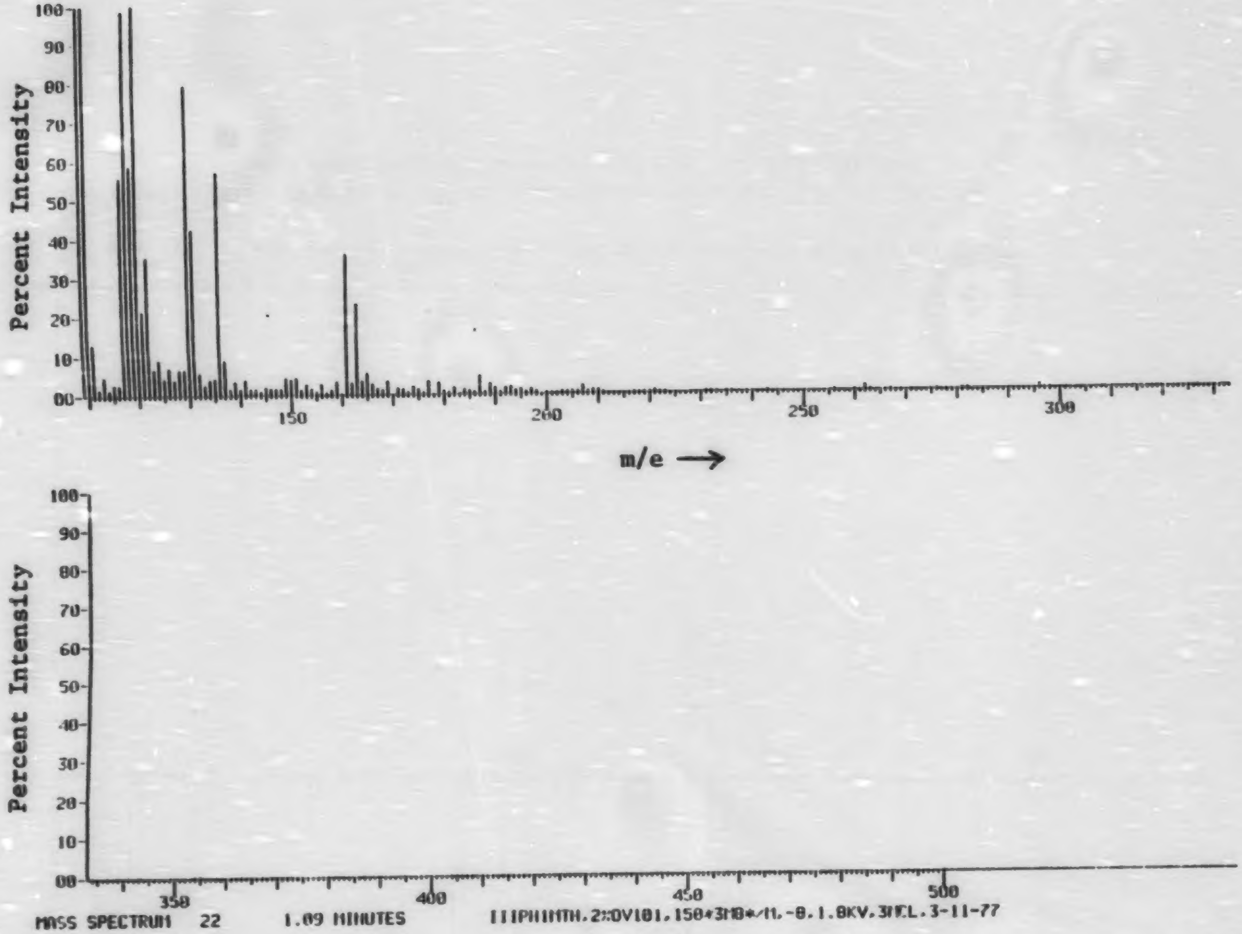


Figure C-32. Mass spectrum of dichloroaniline (M = 161) identified in dimethylsulfate-methylated extract of Philadelphia sludge.

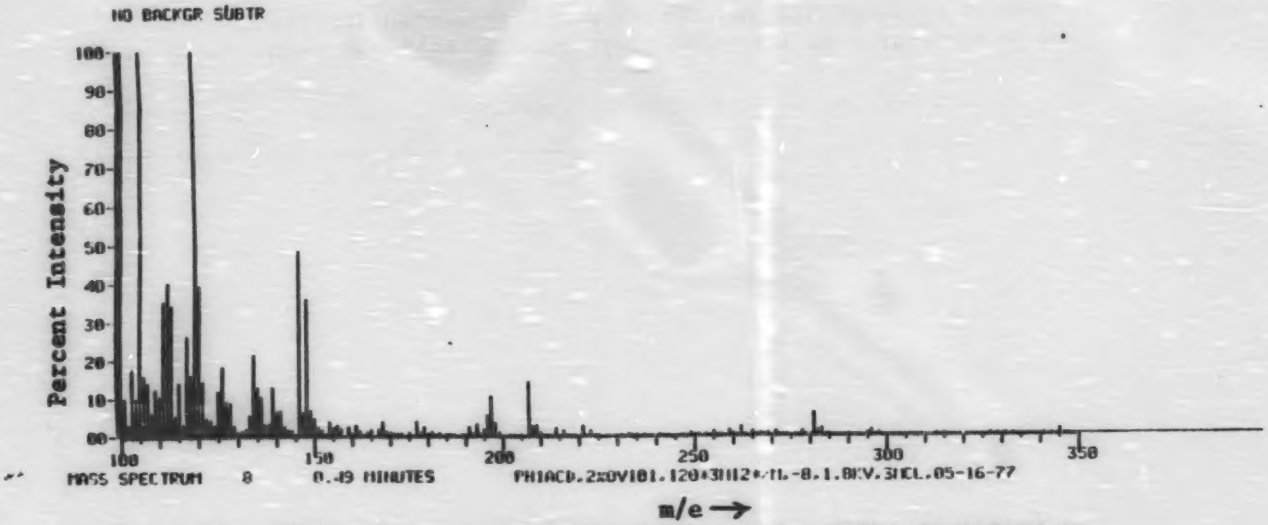


Figure C-33. Mass spectrum of dichlorobenzene (M = 146) identified in diazomethane-methylated extract of Philadelphia sludge.

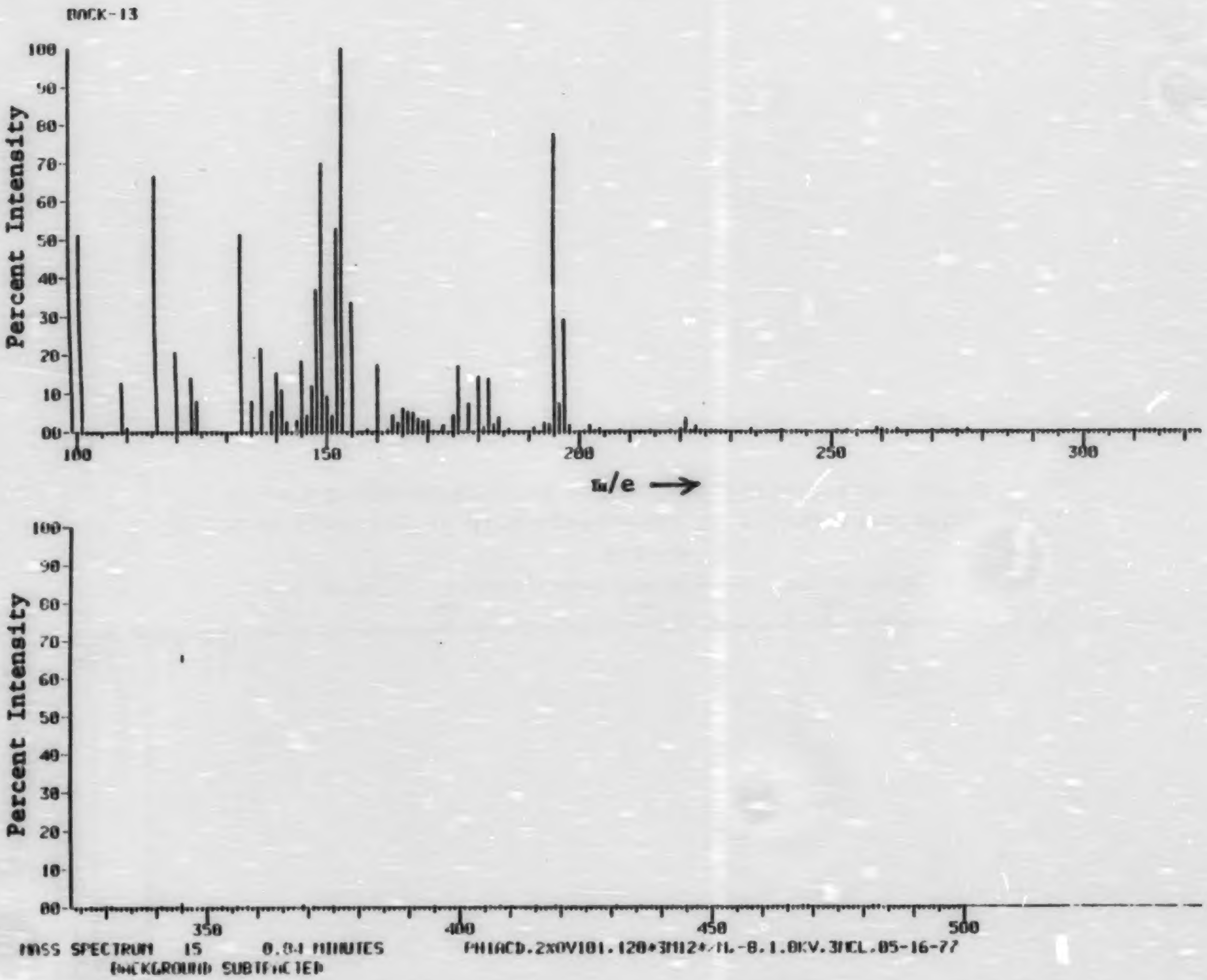


Figure C-34. Mass spectrum of monochloro-compound (M = 195) found in diazomethane-methylated extract of Philadelphia sludge.

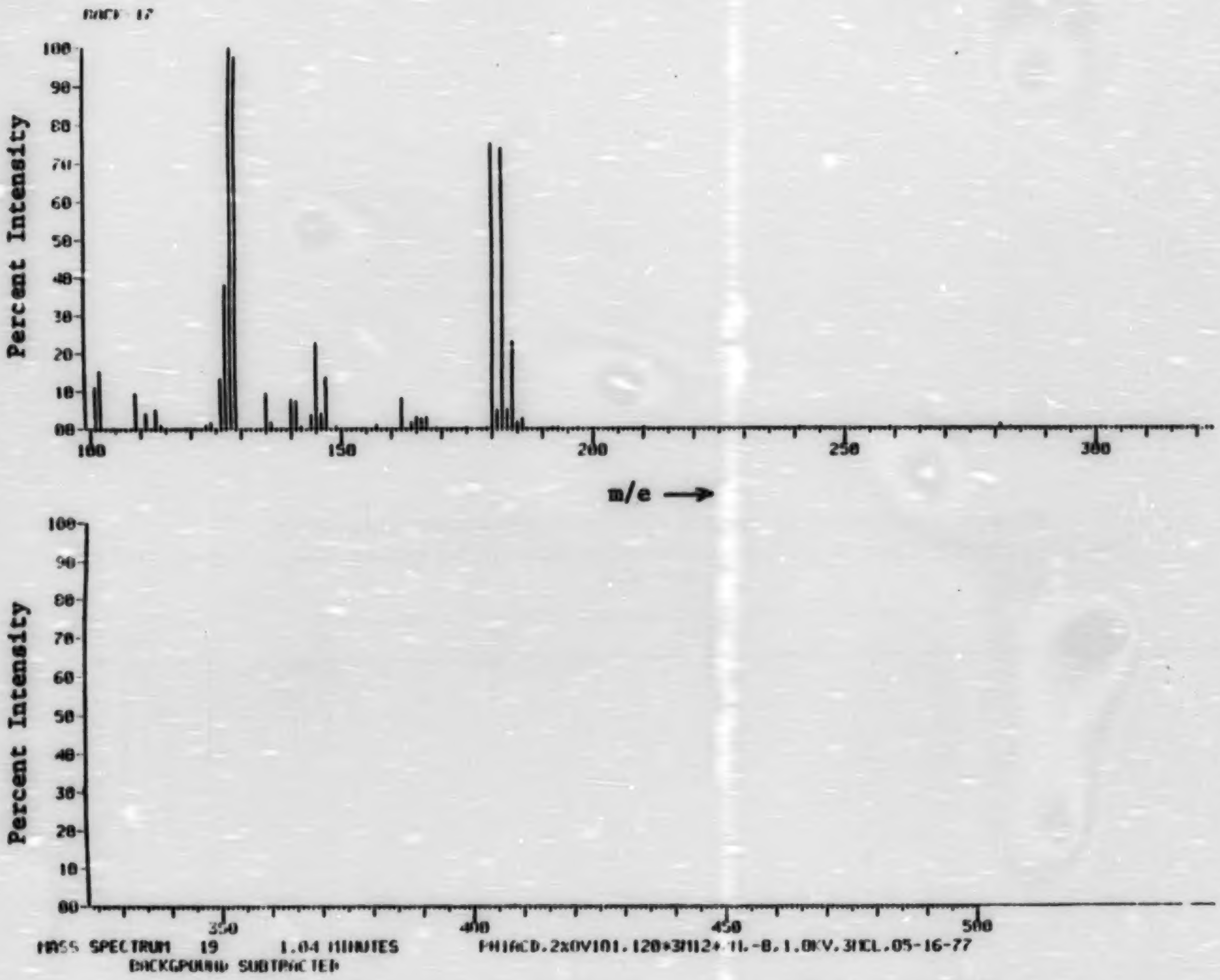


Figure C-35. Mass spectrum of trichlorobenzene (M = 180) identified in diazomethane-methylated extract of Philadelphia sludge.

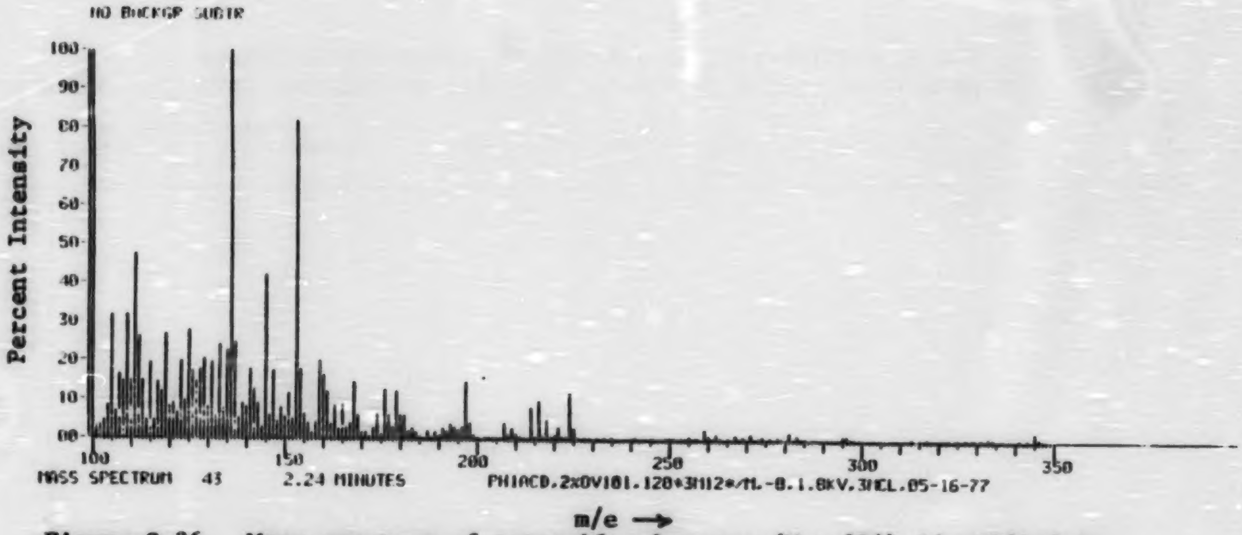


Figure C-36. Mass spectrum of tetrachlorobenzene (M = 214) identified in diazomethane-methylated extract of Philadelphia sludge.

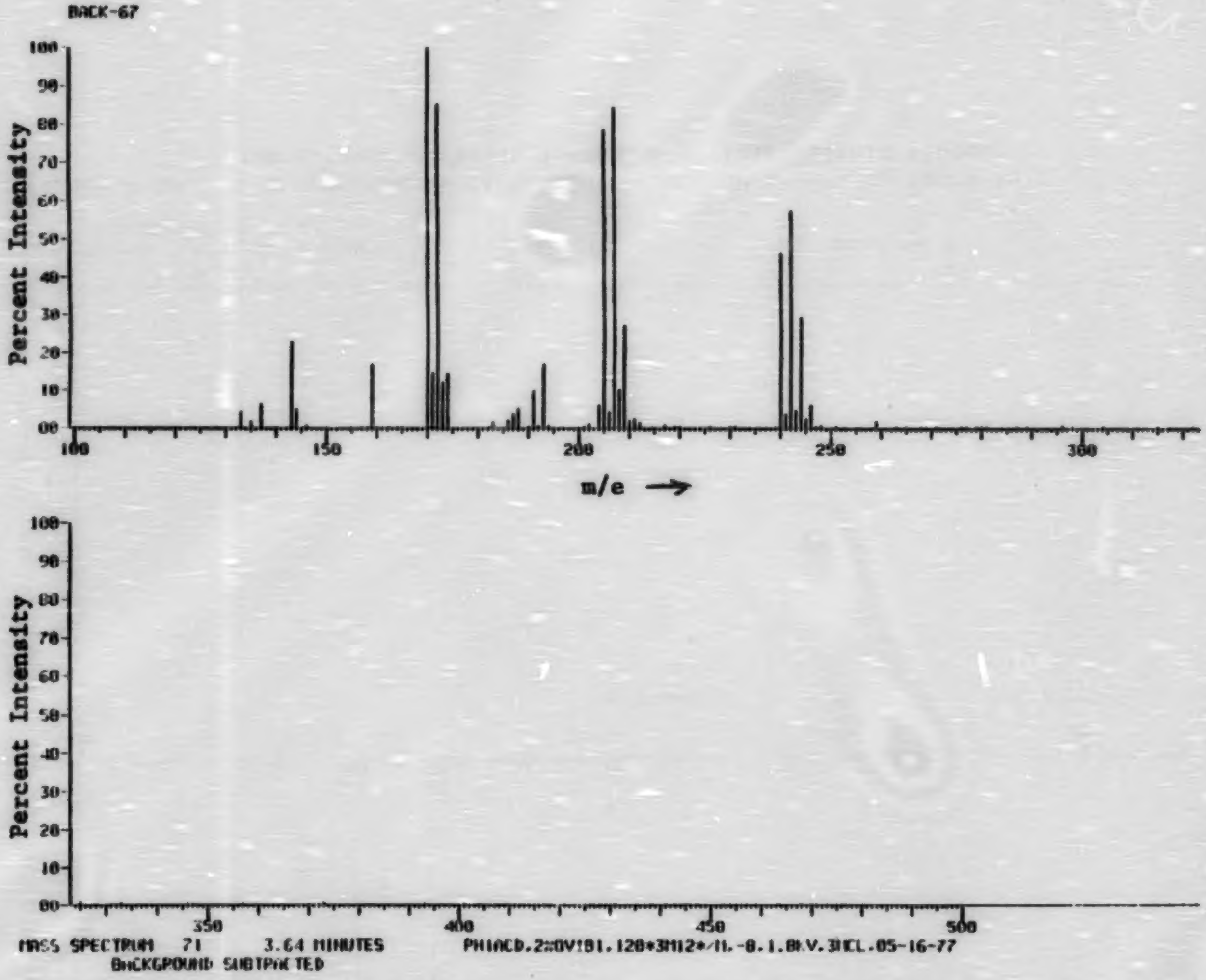


Figure C-37. Mass spectrum of tetrachloro-compound (M = 240) found in diazomethane-methylated extract of Philadelphia sludge.

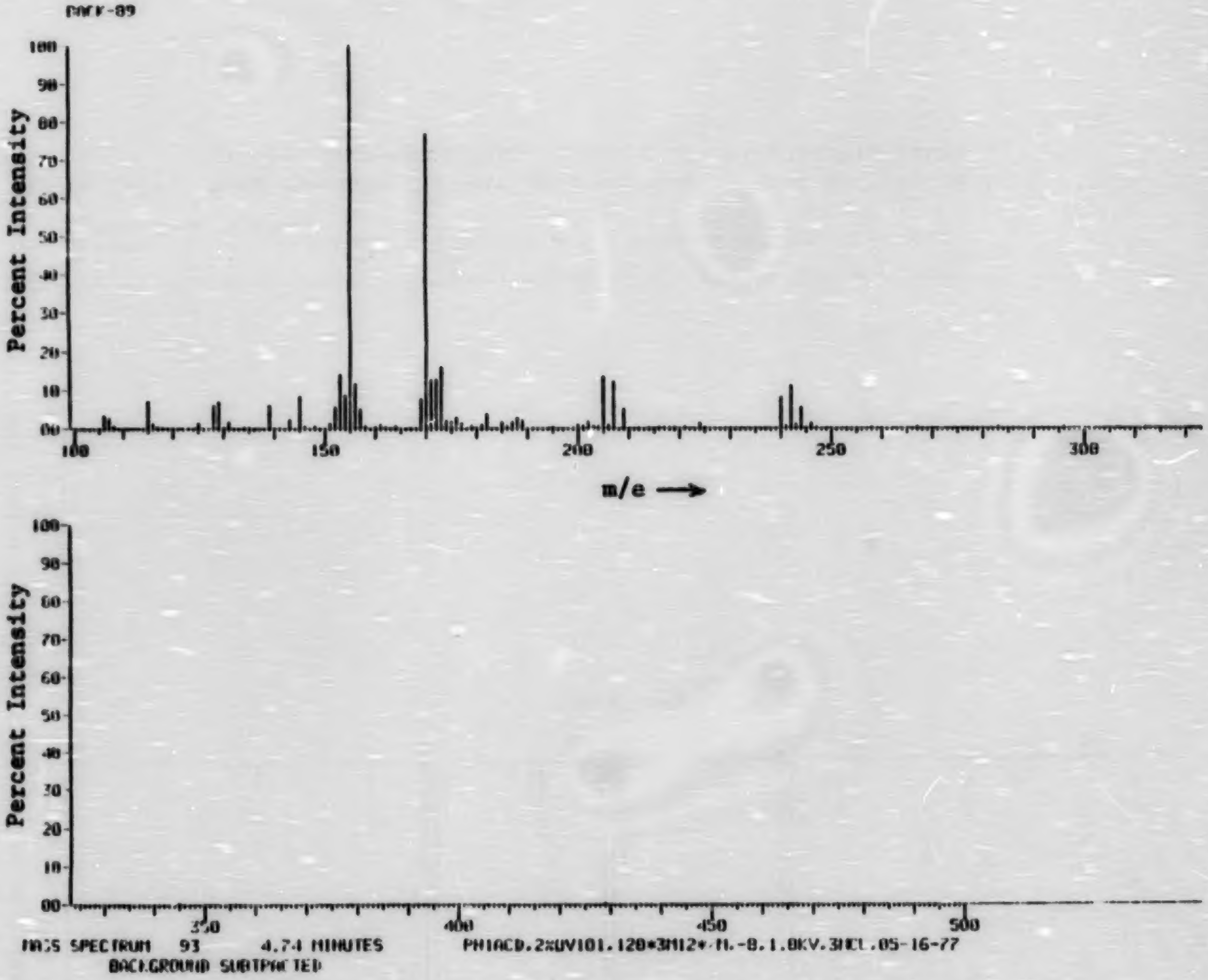


Figure C-38. Mass spectrum of tetrachloro-compound (M = 240) found in diazomethane-methylated extract of Philadelphia sludge.

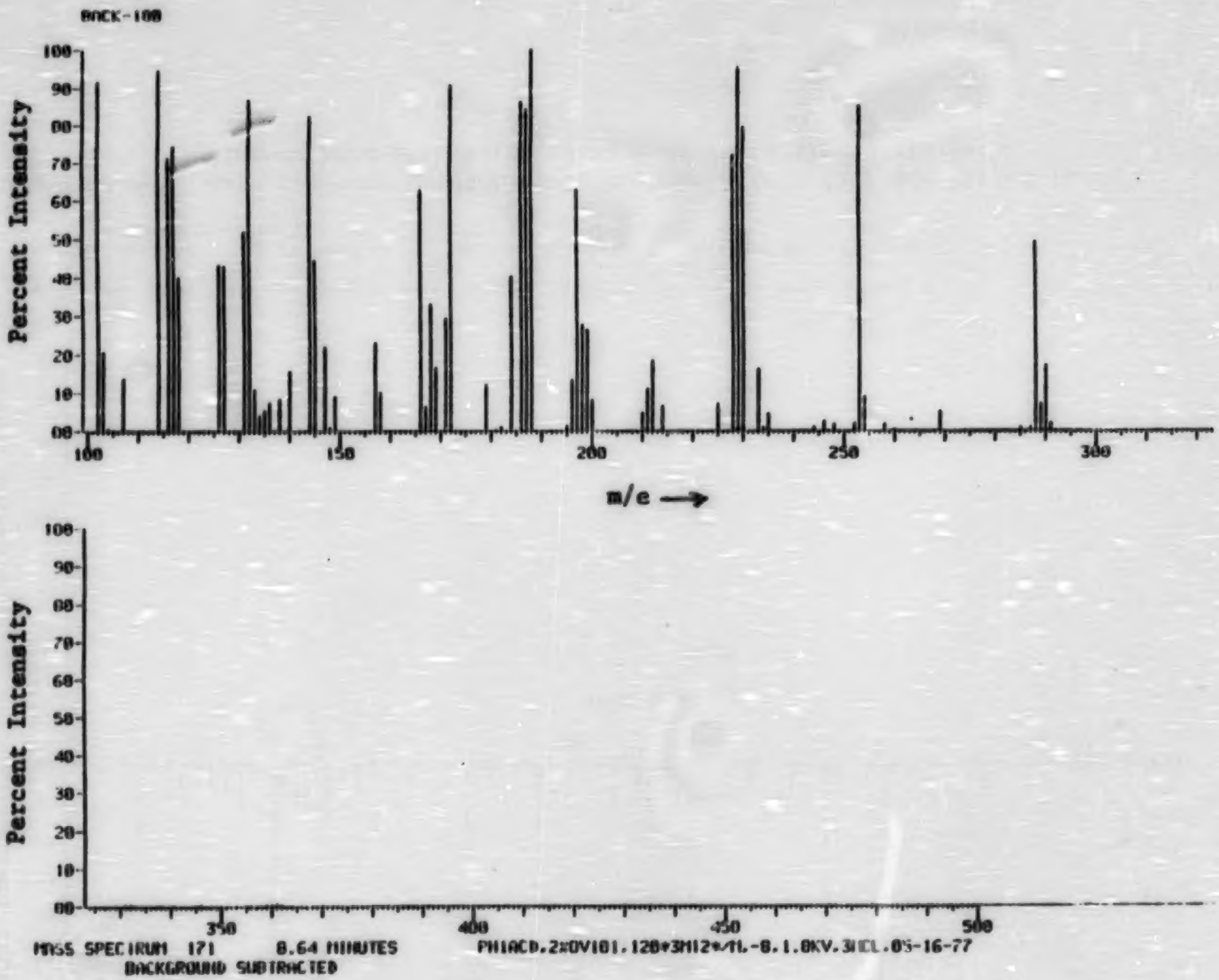


Figure C-39. Mass spectrum of monochloro-compound (M = 288) found in diazomethane-methylated extract of Philadelphia sludge.

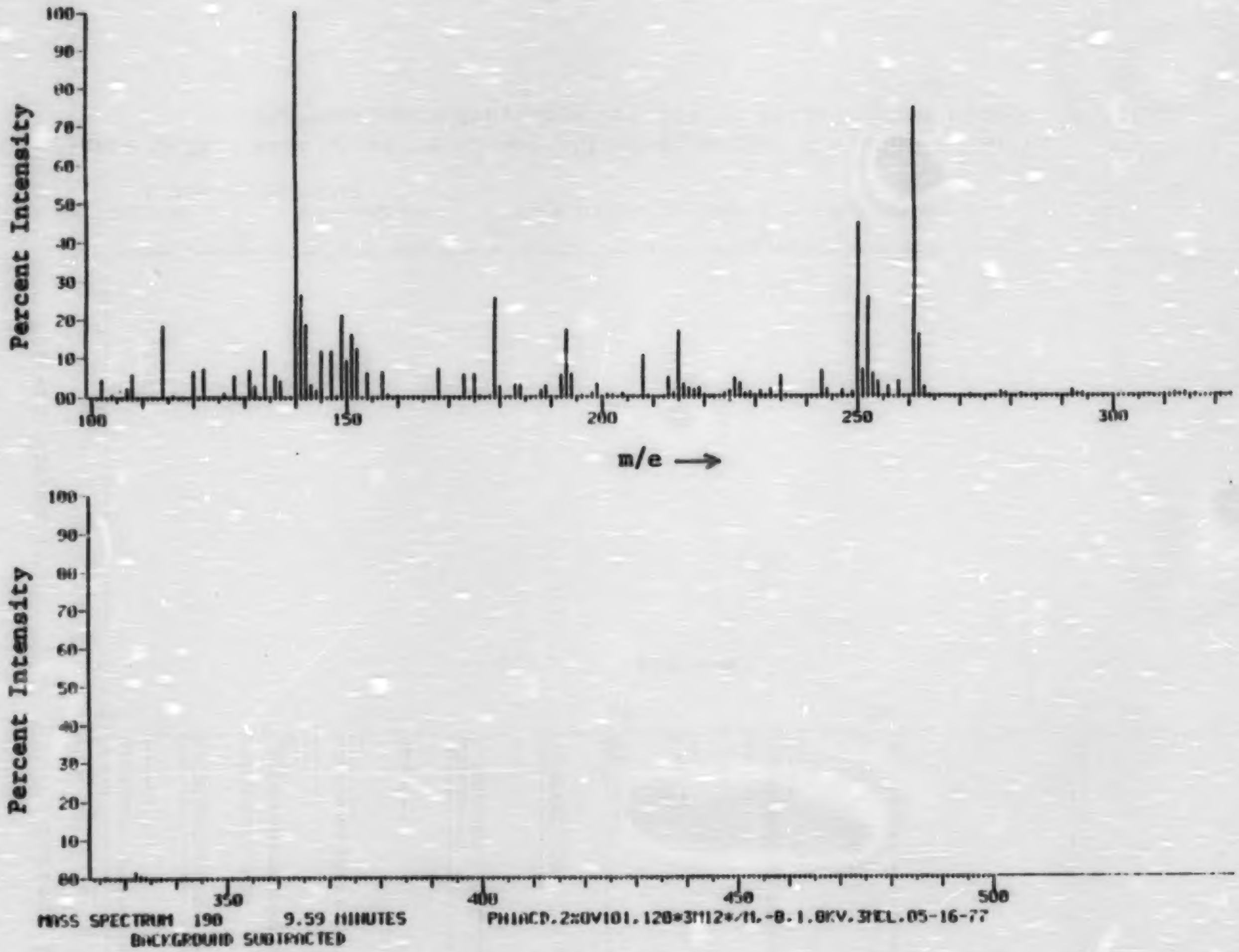


Figure C-40. Mass spectrum of dichlorobenzophenone (M = 250) identified in diazomethane-methylated extract of Philadelphia sludge.

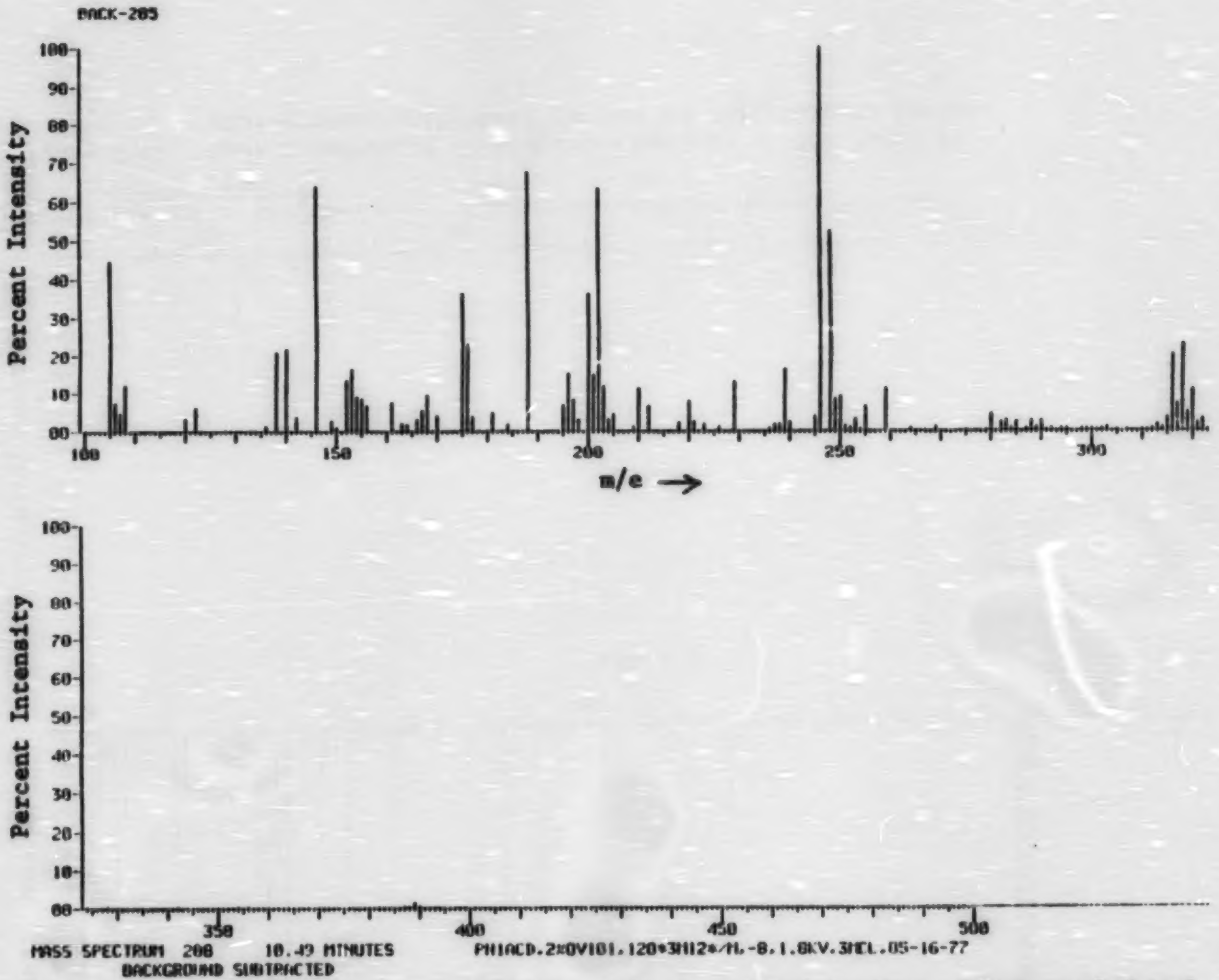


Figure C-41. Mass spectrum of DDE (M = 316) identified in diazomethane-methylated extract of Philadelphia sludge.

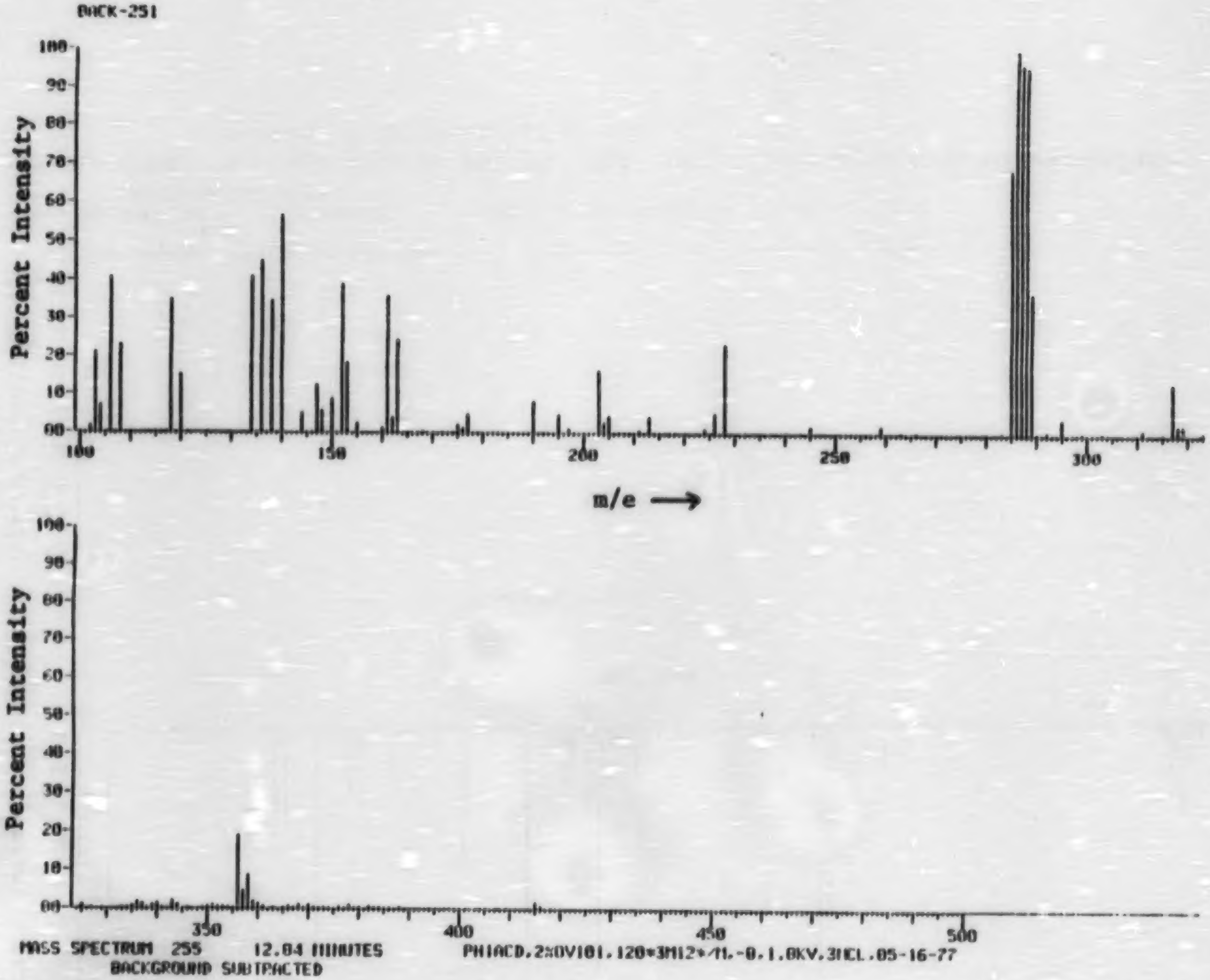


Figure C-42. Mass spectrum of dichloro-compound (M = 356) found in diazomethane-methylated extract of Philadelphia sludge.

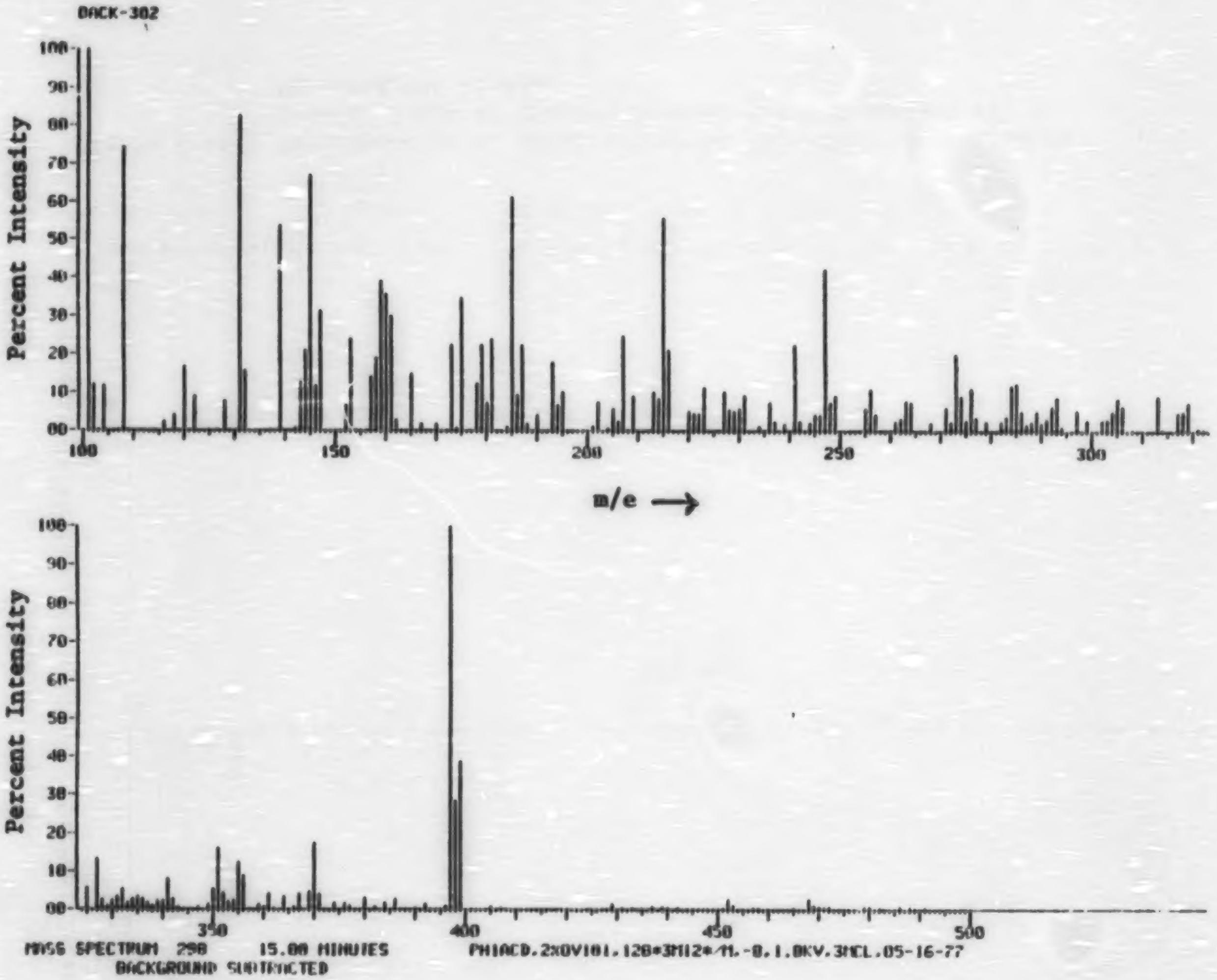


Figure C-43. Mass spectrum of monochloro-compound (M = 397) found in diazomethane-methylated extract of Philadelphia sludge.

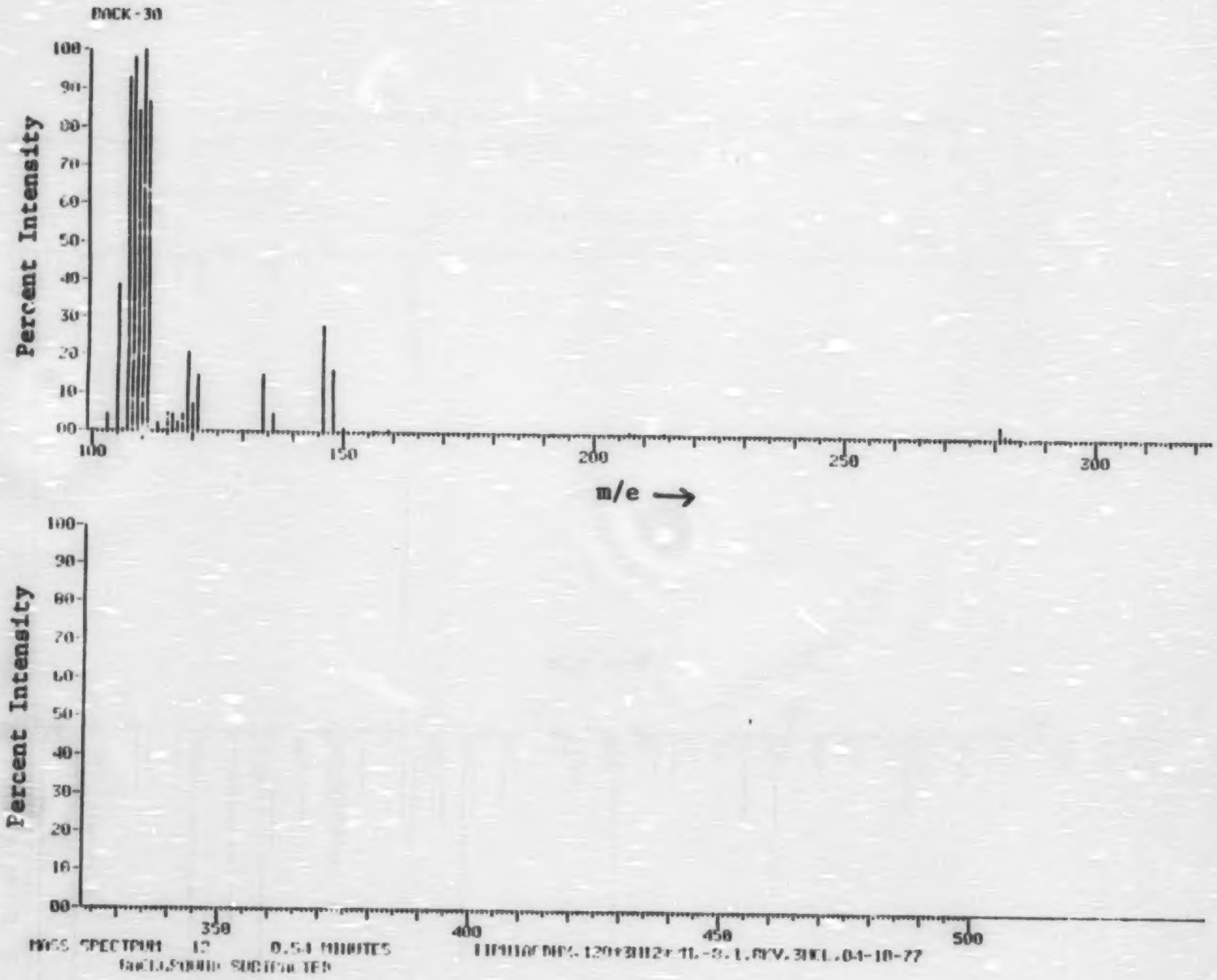


Figure C-44. Mass spectrum of dichlorobenzene (M = 146) identified in hexane eluate of diazomethane-methylated extract of Philadelphia sludge.

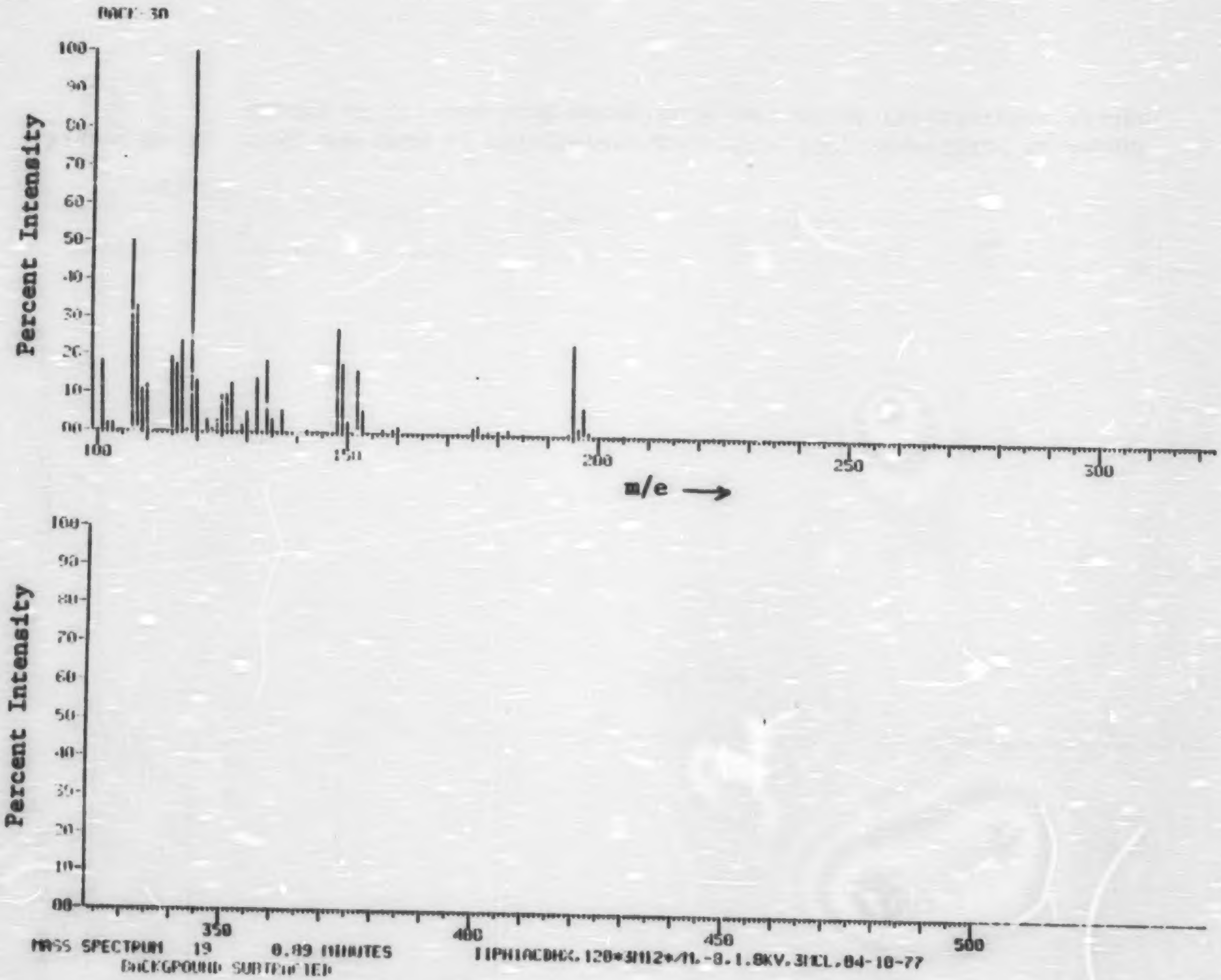


Figure C-45. Mass spectrum of monochloro-compound (M = 195) found in hexane eluate of diazomethane-methylated extract of Philadelphia sludge.

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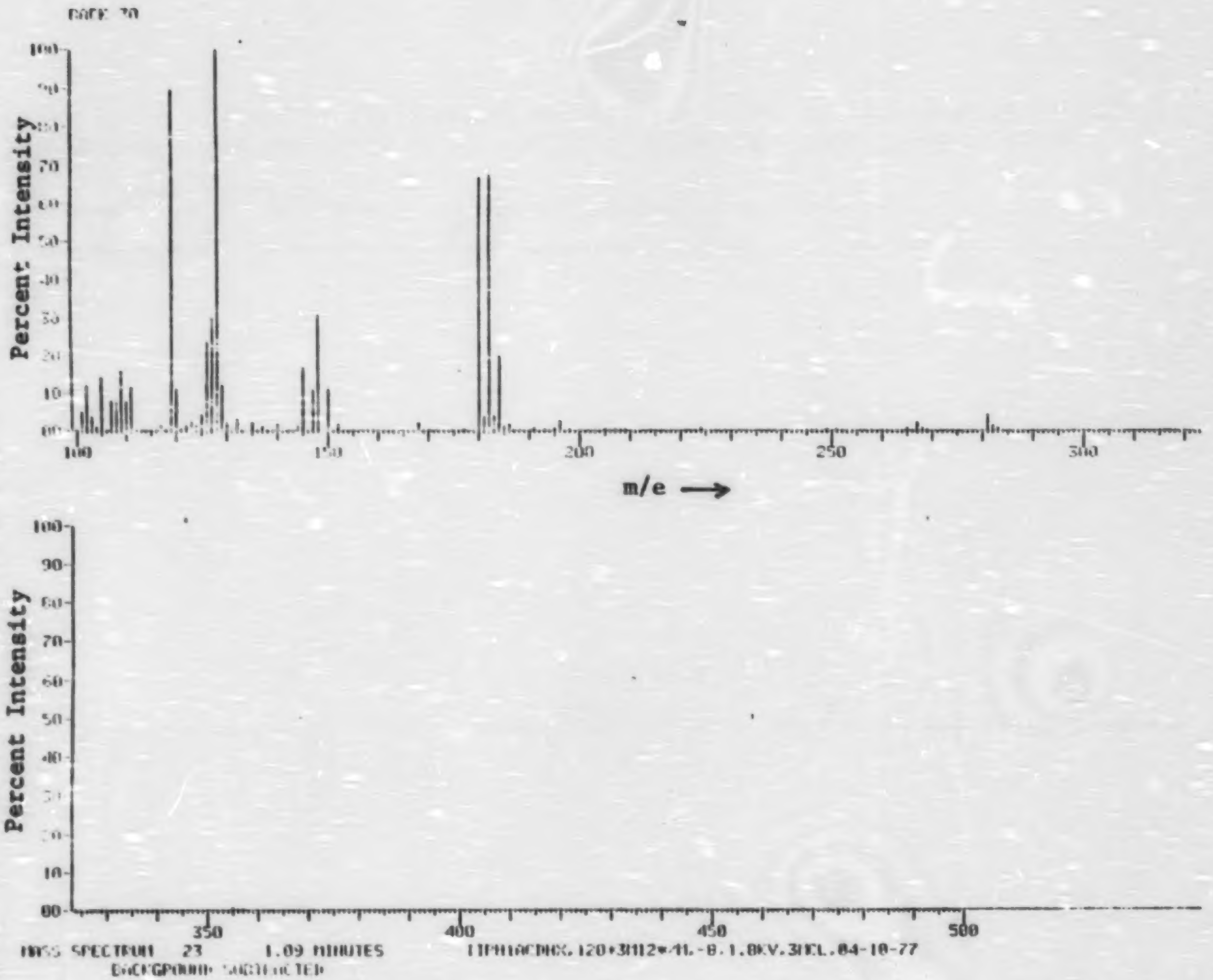

Figure C-46. Mass spectrum of trichlorobenzene (M = 180) identified in hexane eluate of diazomethane-methylated extract of Philadelphia sludge.

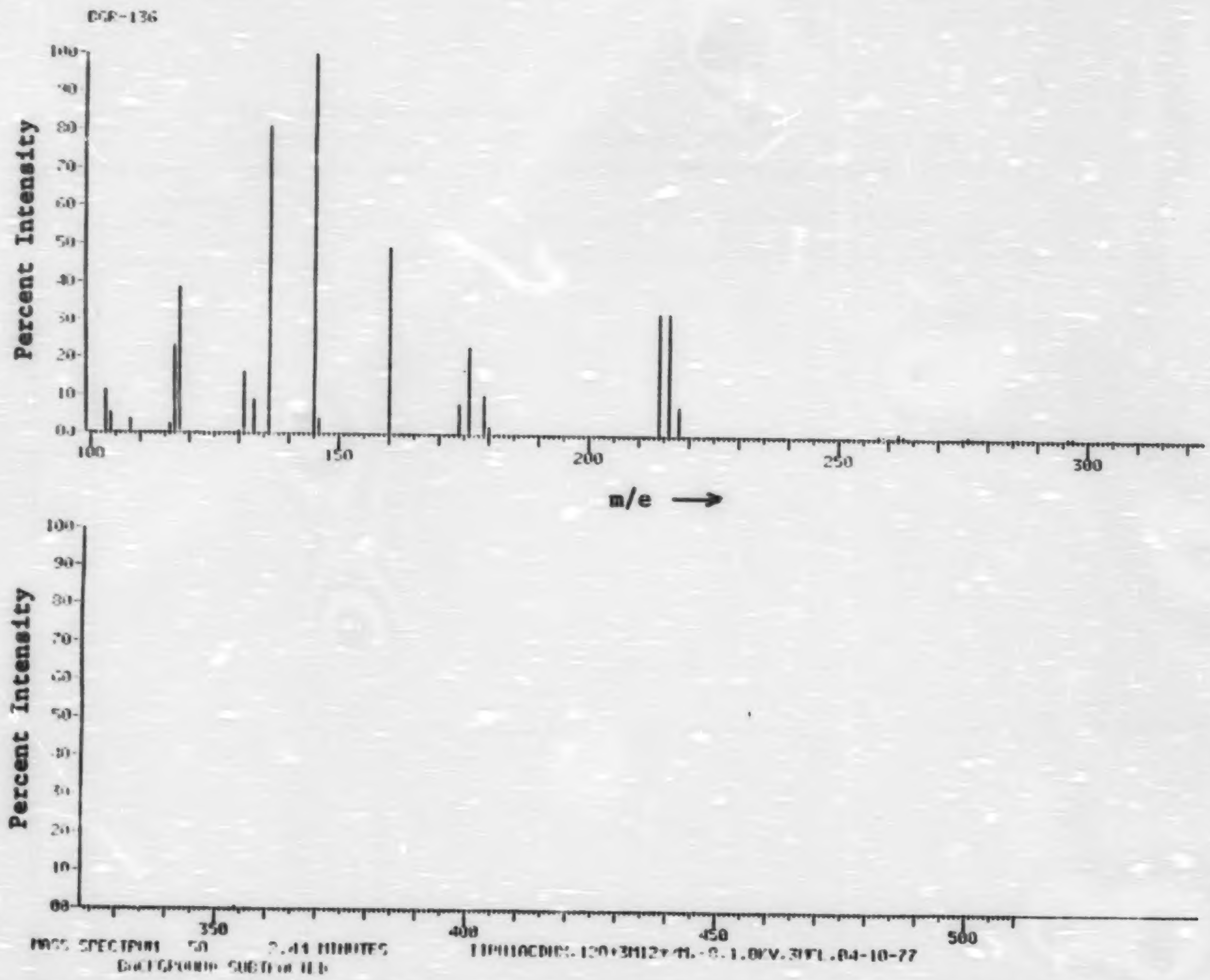

Figure C-47. Mass spectrum of tetrachlorobenzene (M = 214) identified in hexane eluate of diazomethane-methylated extract of Philadelphia sludge.

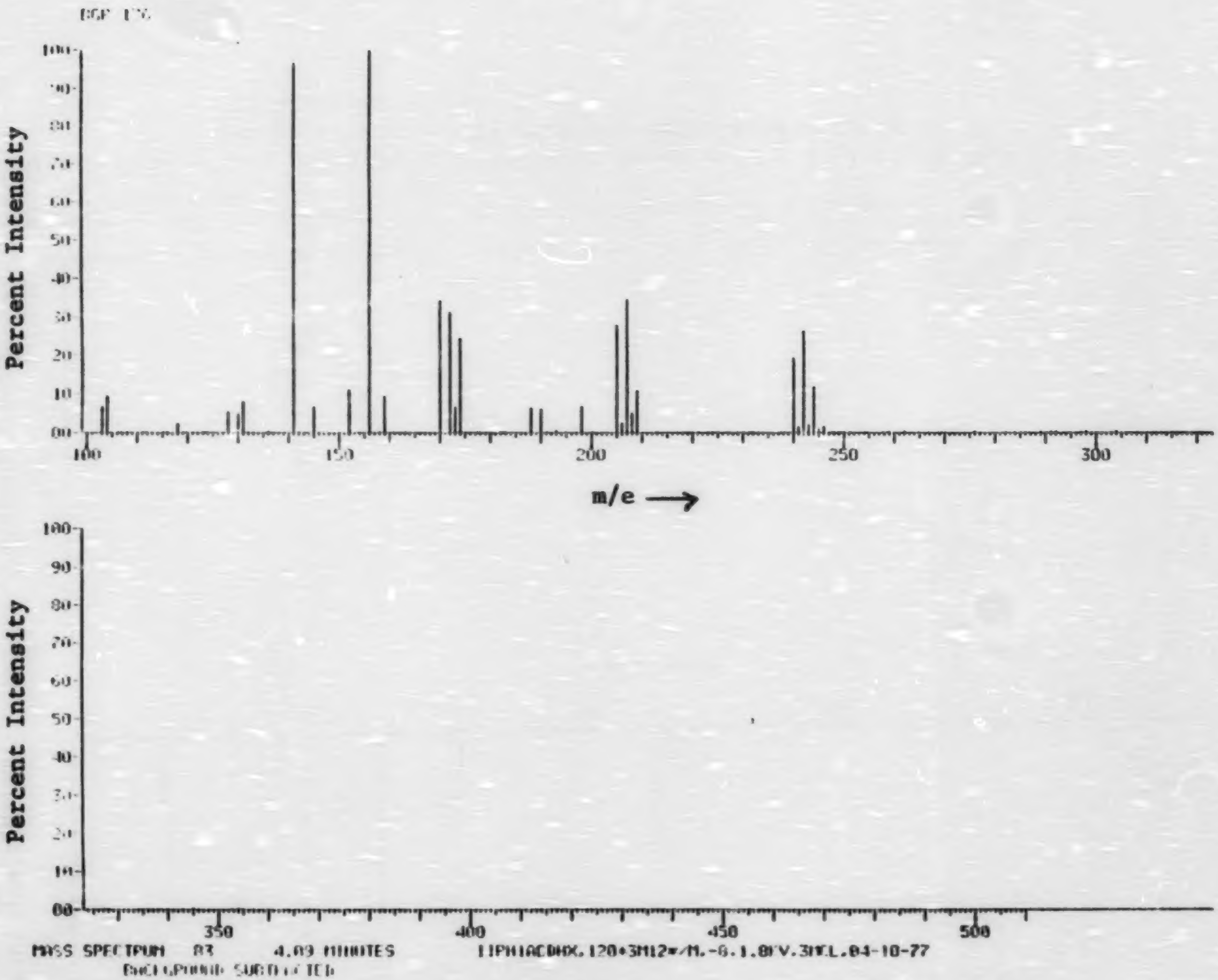

Figure C-48. Mass spectrum of tetrachloro-compound (M = 240) found in hexane eluate of diazomethane-methylated extract of Philadelphia sludge.

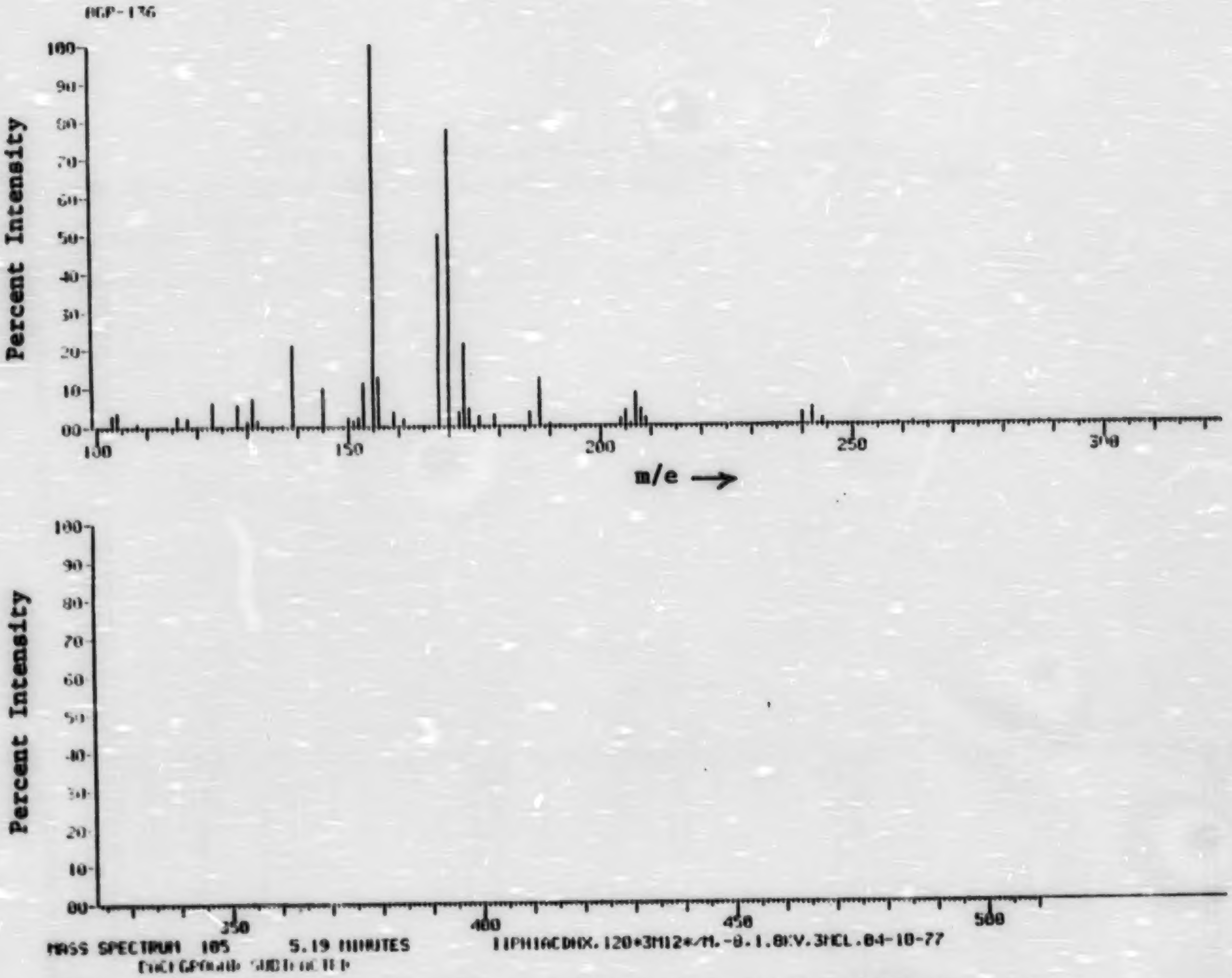

Figure C-49. Mass spectrum of tetrachloro-compound (M = 240) found in hexane eluate of diazomethane-methylated extract of Philadelphia sludge.

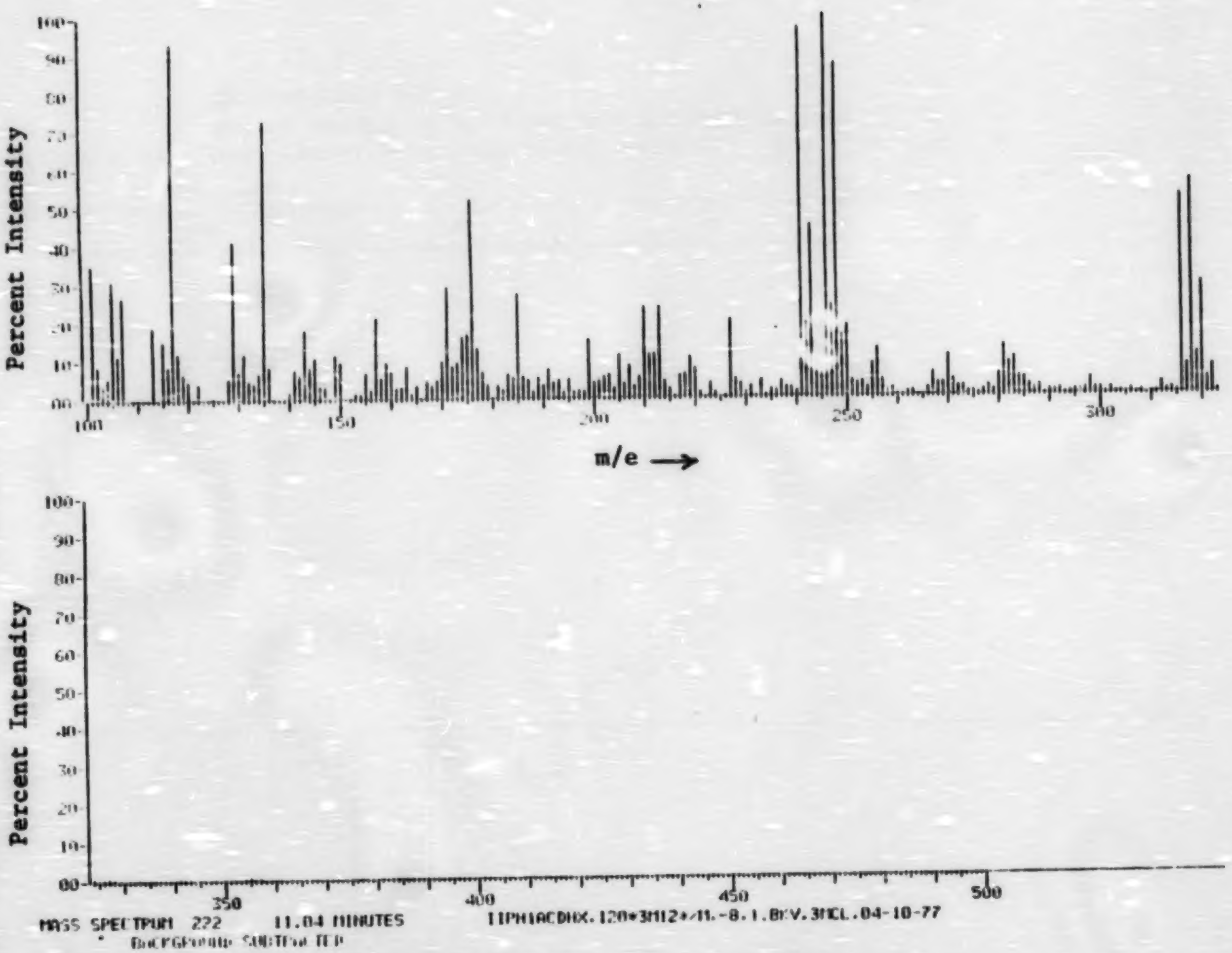

Figure C-50. Mass spectrum of DDE (M = 316) identified in hexane eluate of diazomethane-methylated extract of Philadelphia sludge.

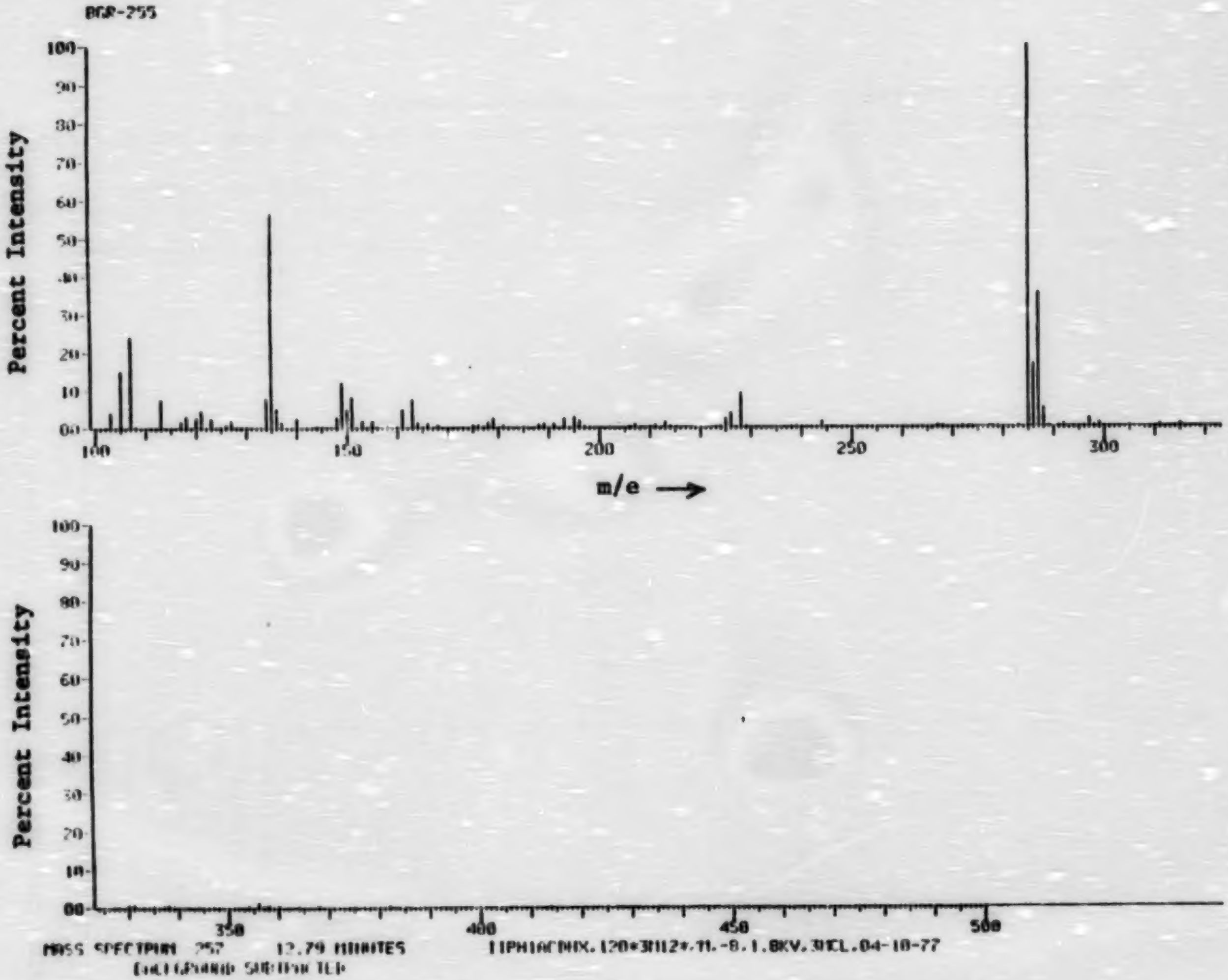

Figure C-51. Mass spectrum of monochloro-compound (M = 285) found in hexane eluate of diazomethane-methylated extract of Philadelphia sludge.

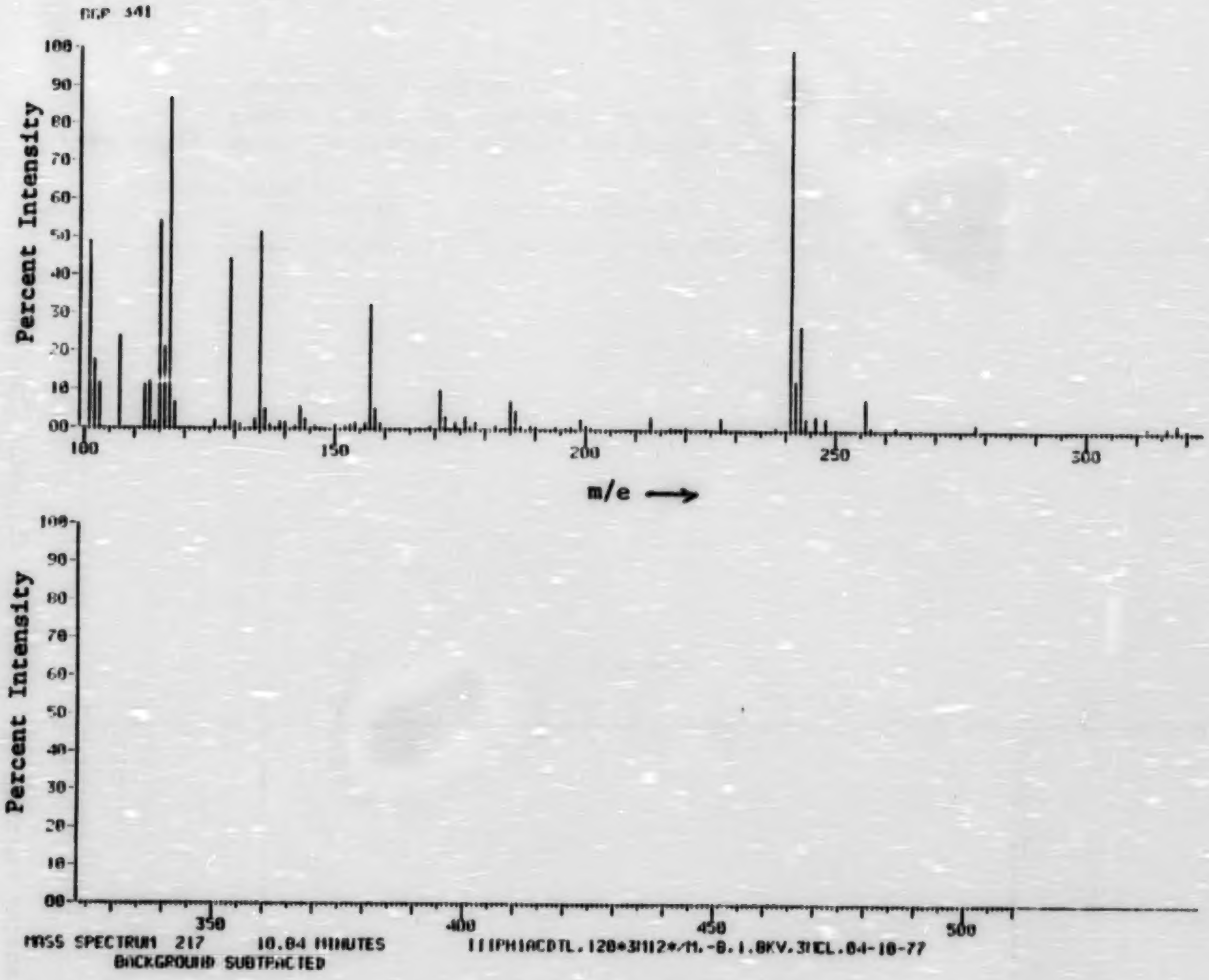

Figure C-52. Mass spectrum of monochloro-compound (M = 241) found in toluene eluate of diazomethane-methylated extract of Philadelphia sludge.

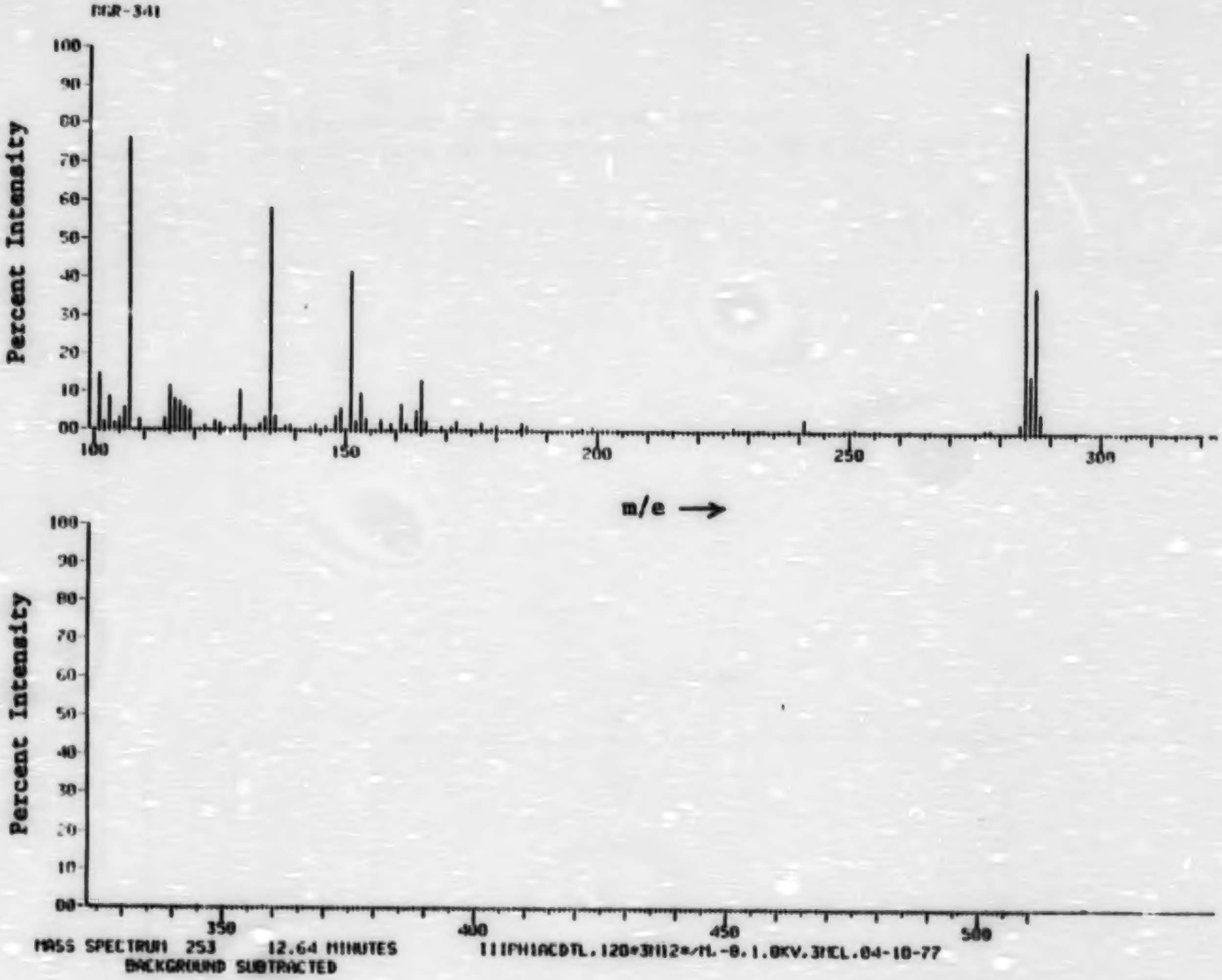

Figure C-53. Mass spectrum of monochloro-compound (M = 285) found in toluene eluate of diazomethane-methylated acid extract of Philadelphia sludge.

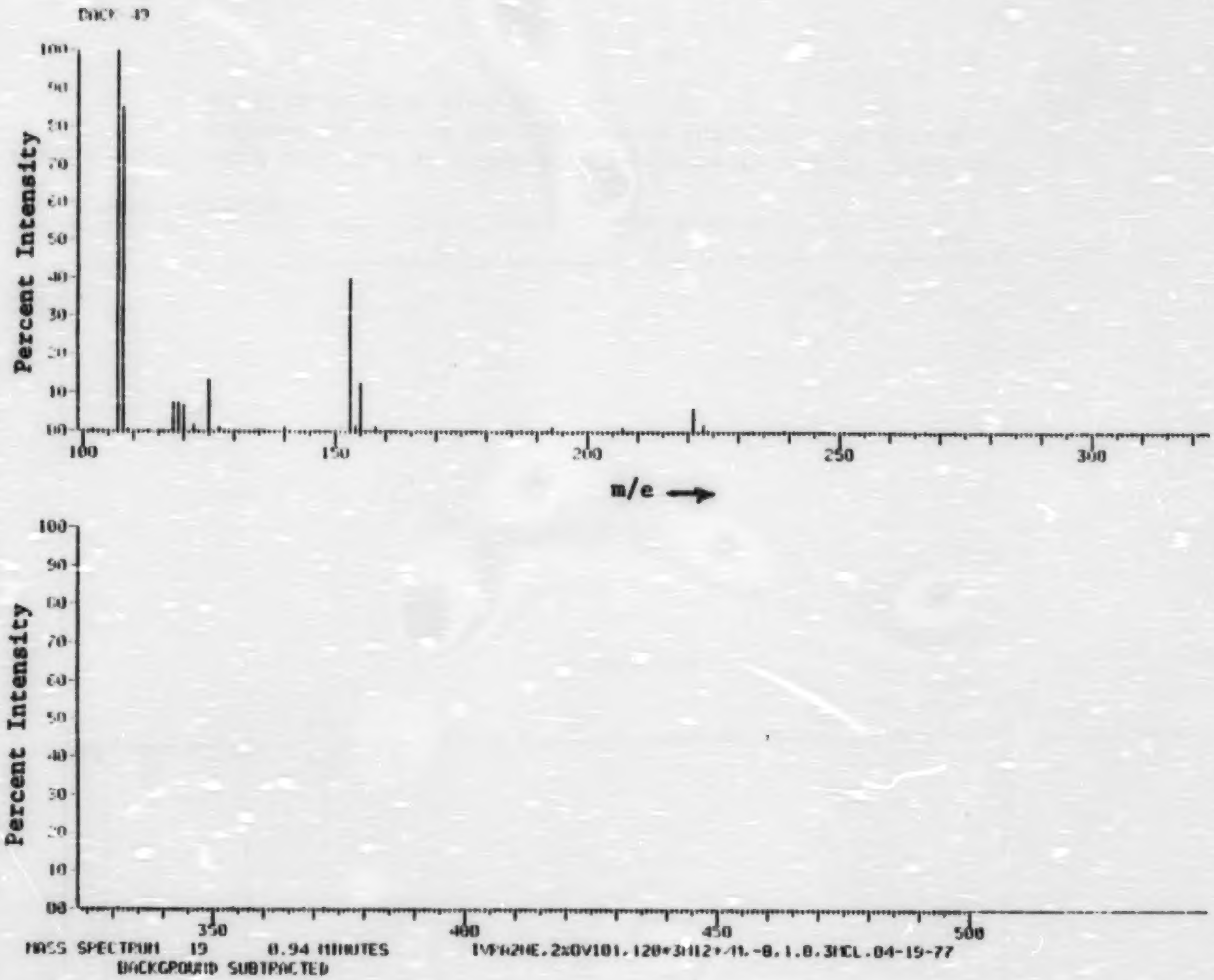

Figure C-54. Mass spectrum of monochloro-compound (M = 221) found in neutral extract of Raleigh sludge.

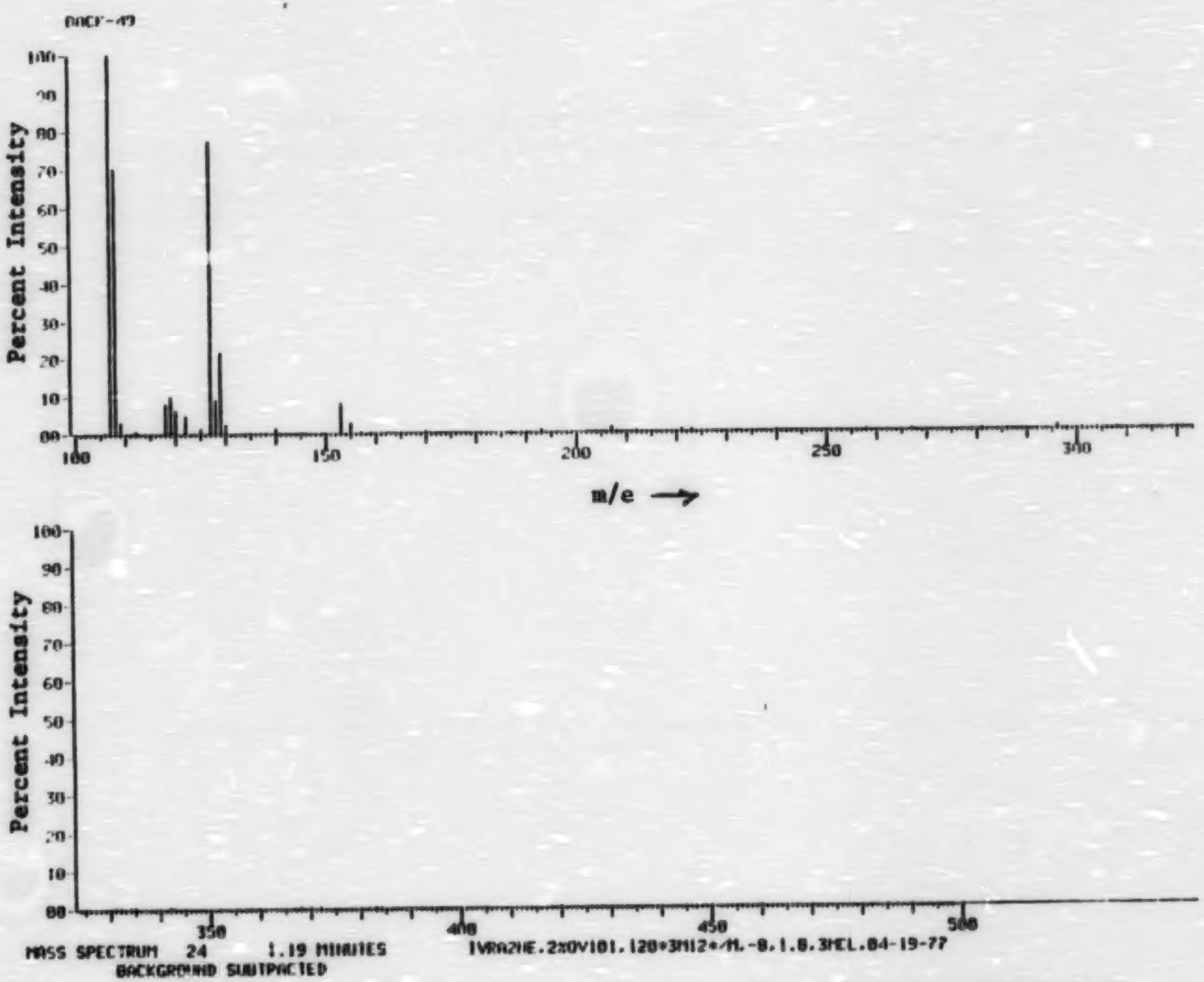

Figure C-55. Mass spectrum of chloroaniline (M = 127) tentatively identified in neutral extract of Raleigh sludge.

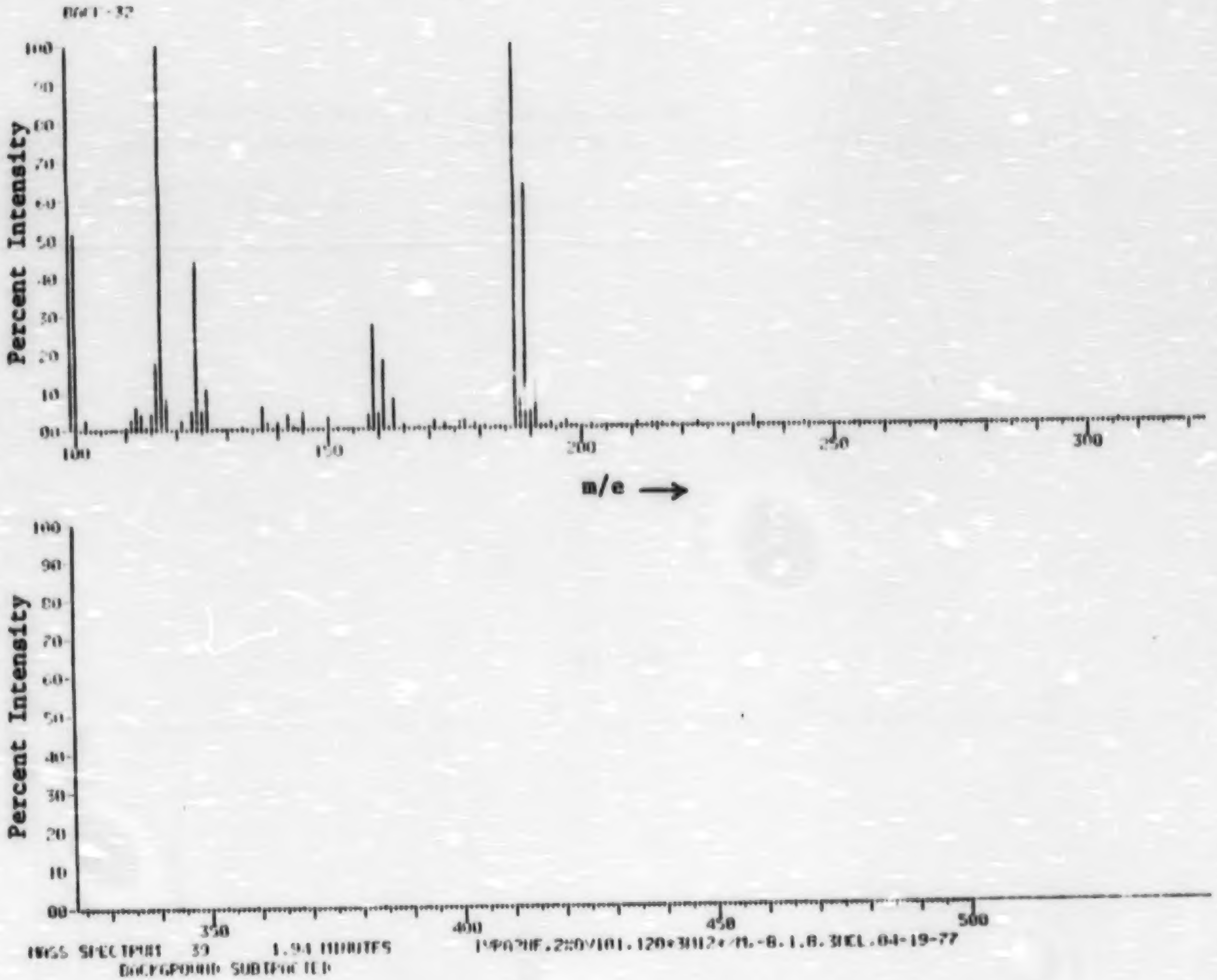

Figure C-56. Mass spectrum of dichloro-compound (M = 187) found in neutral extract of Raleigh sludge.

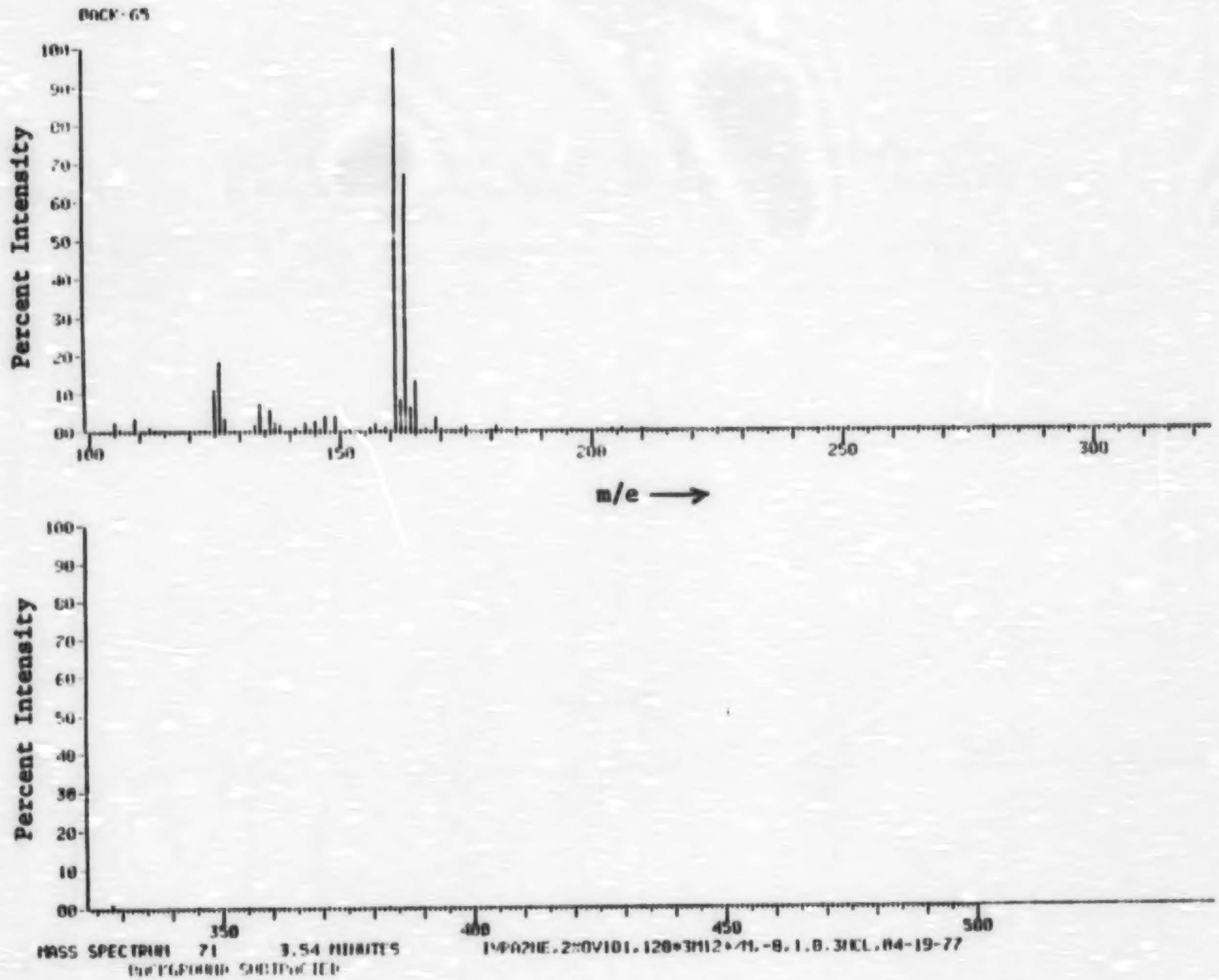

Figure C-57. Mass spectrum of dichloroaniline (M = 161) identified in neutral extract of Raleigh sludge.

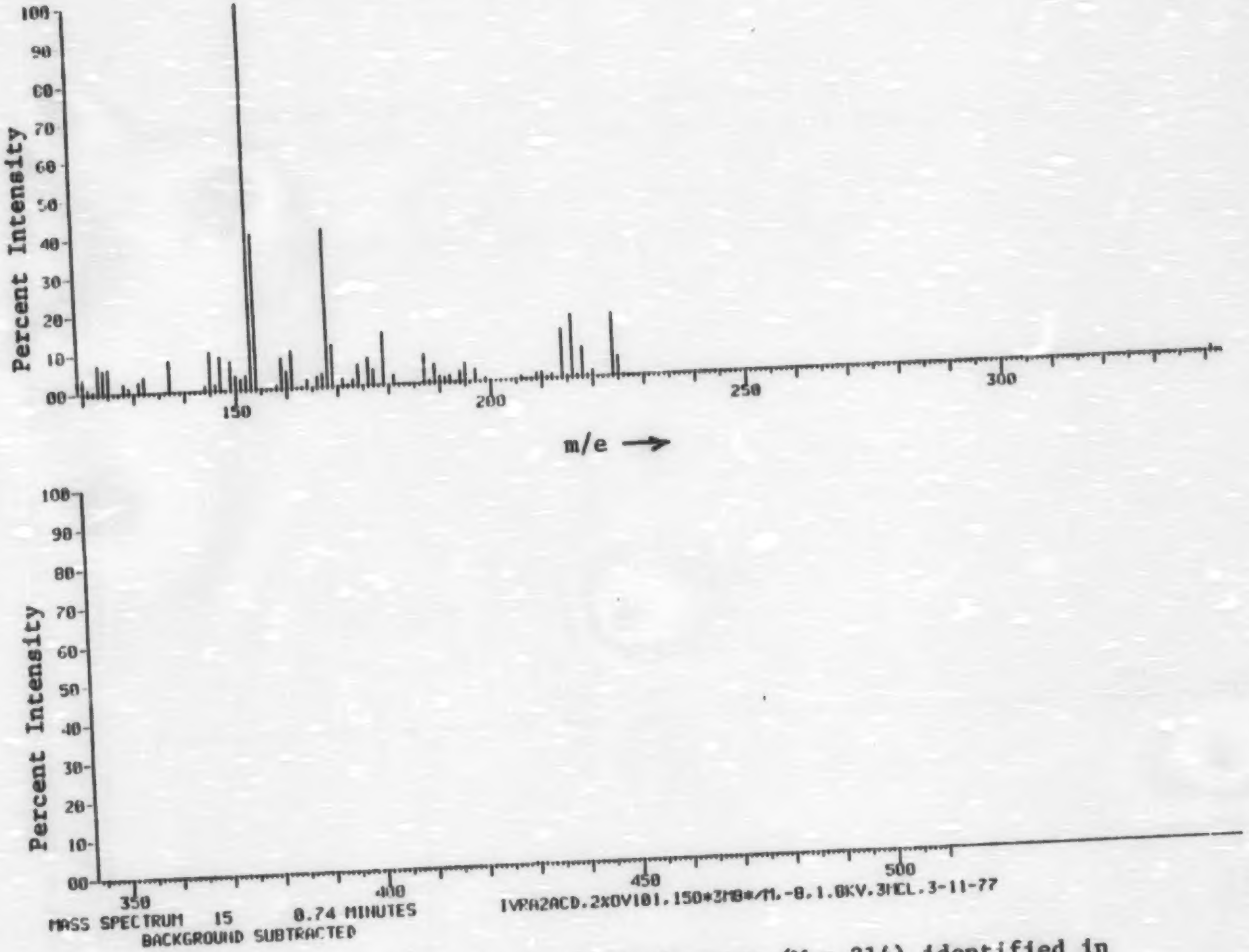

Figure C-58. Mass spectrum of tetrachlorobenzene (M = 214) identified in diazomethane-methylated extract of Raleigh sludge.

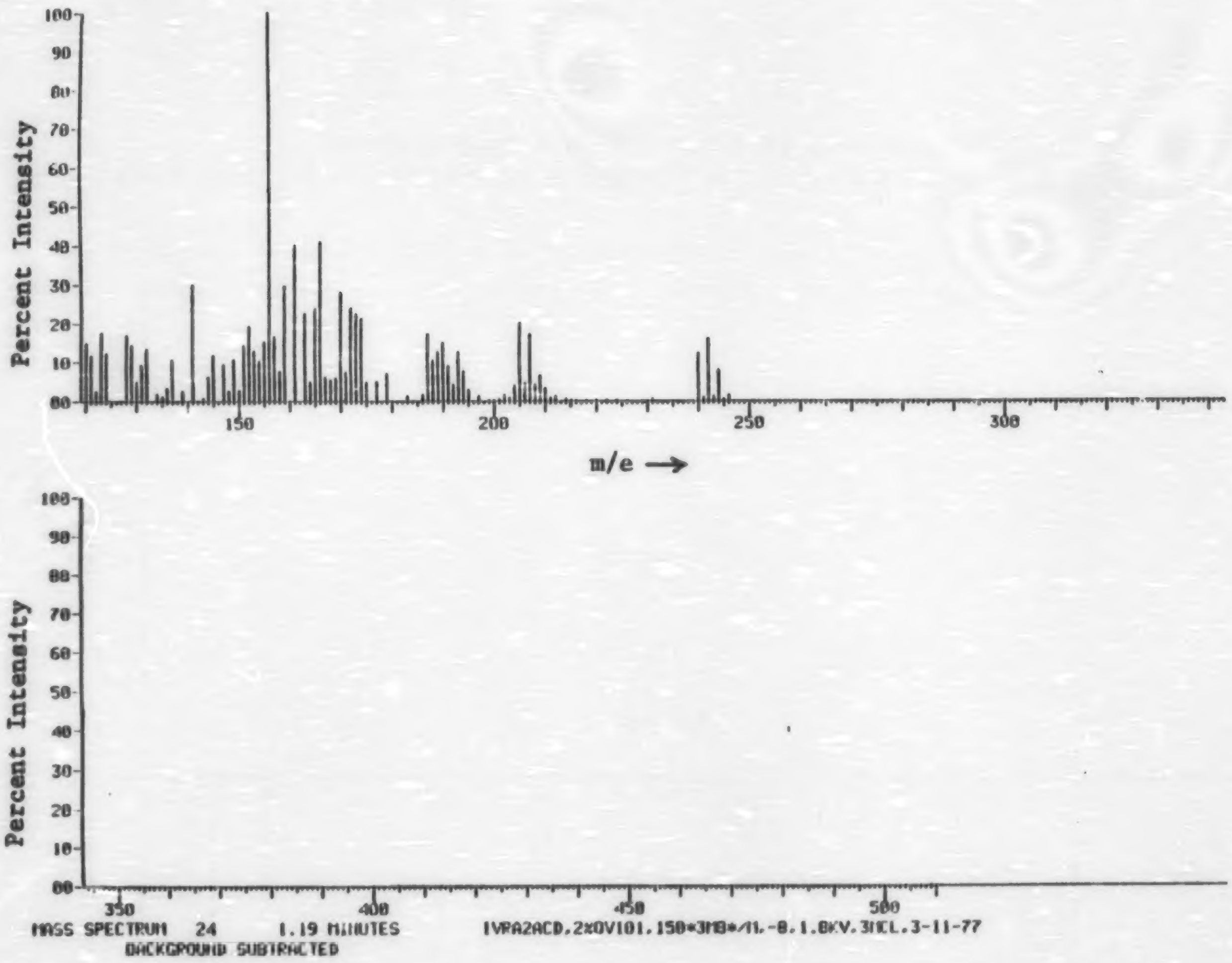

Figure C-59. Mass spectrum of tetrachloro-compound (M = 240) found in diazomethane-methylated extract of Raleigh sludge.

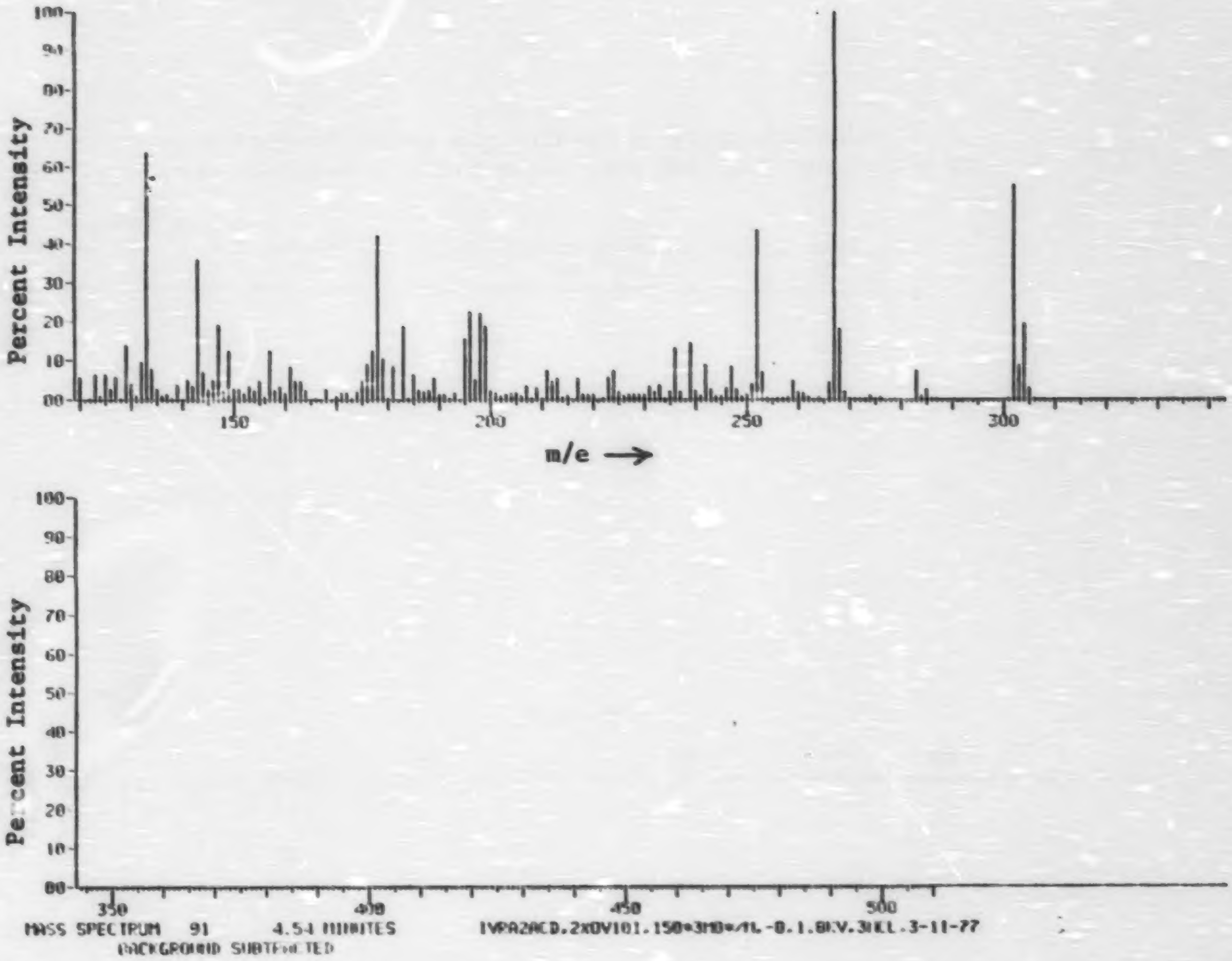

Figure C-60. Mass spectrum of monochloro-compound (M = 302) found in diazomethane-methylated extract of Raleigh sludge.

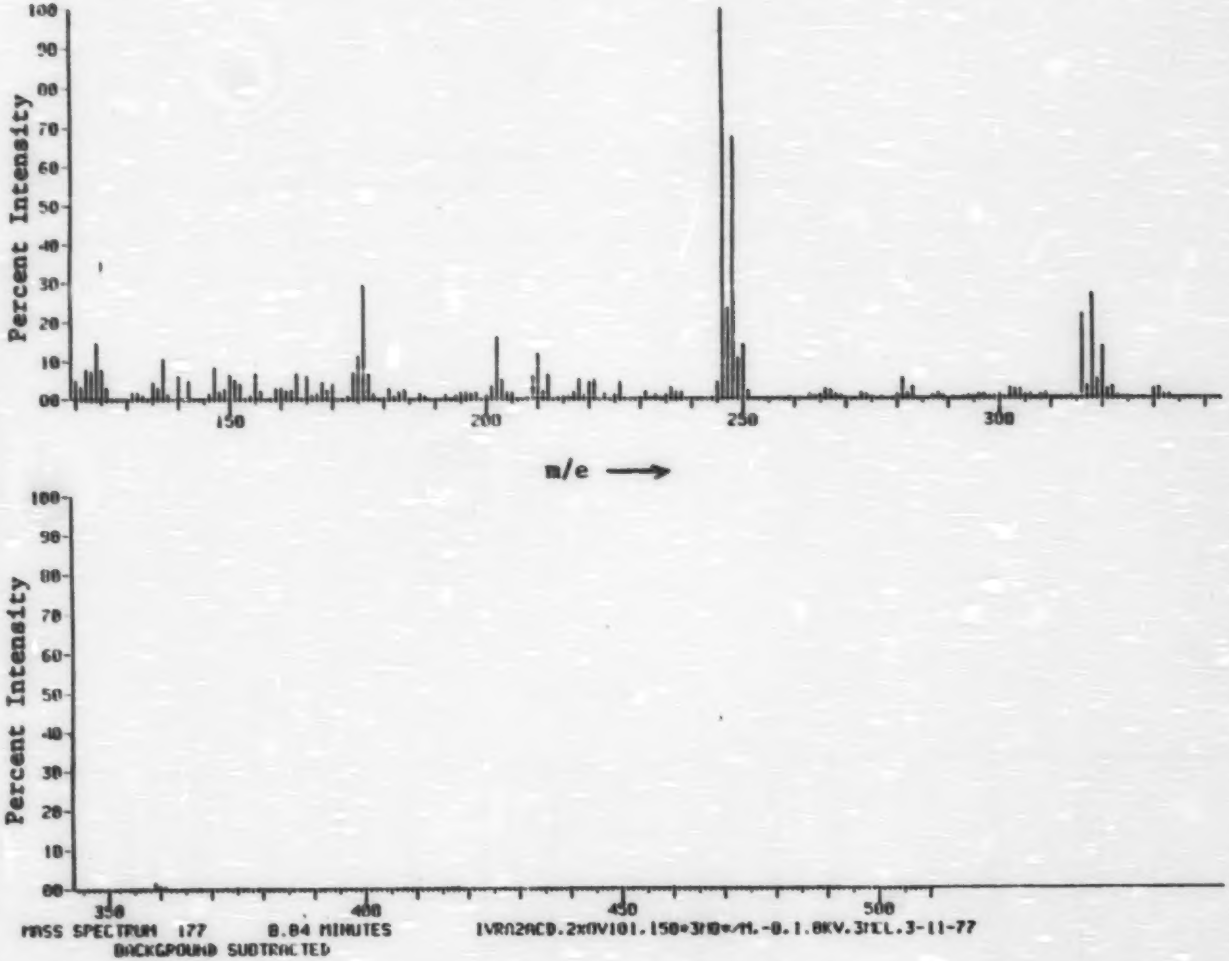

Figure C-61. Mass spectrum of DDE (M = 316) identified in diazomethane-methylated extract of Raleigh sludge.

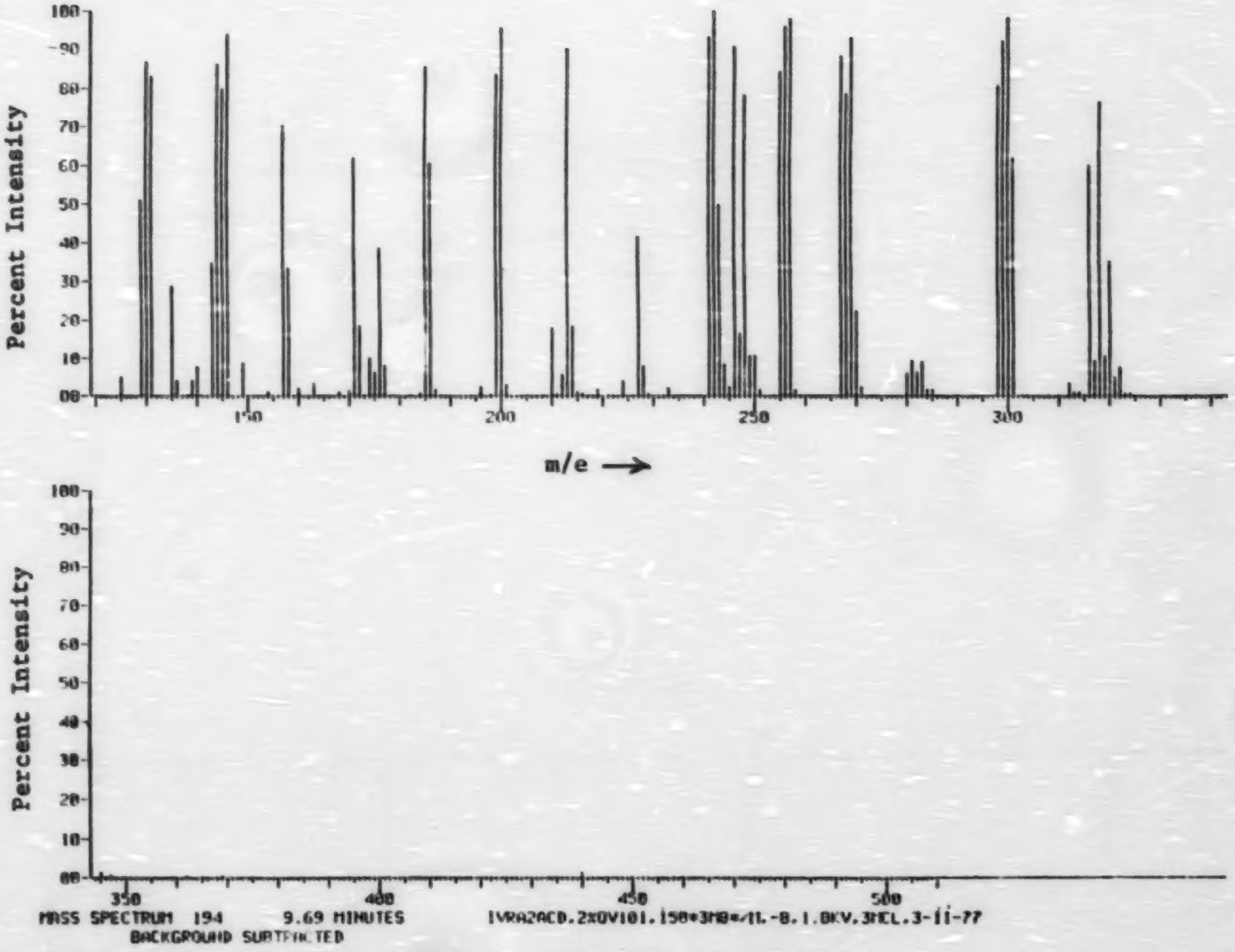

Figure C-62. Mass spectrum of DDE (M = 314) identified in diazomethane-methylated extract of Raleigh sludge.

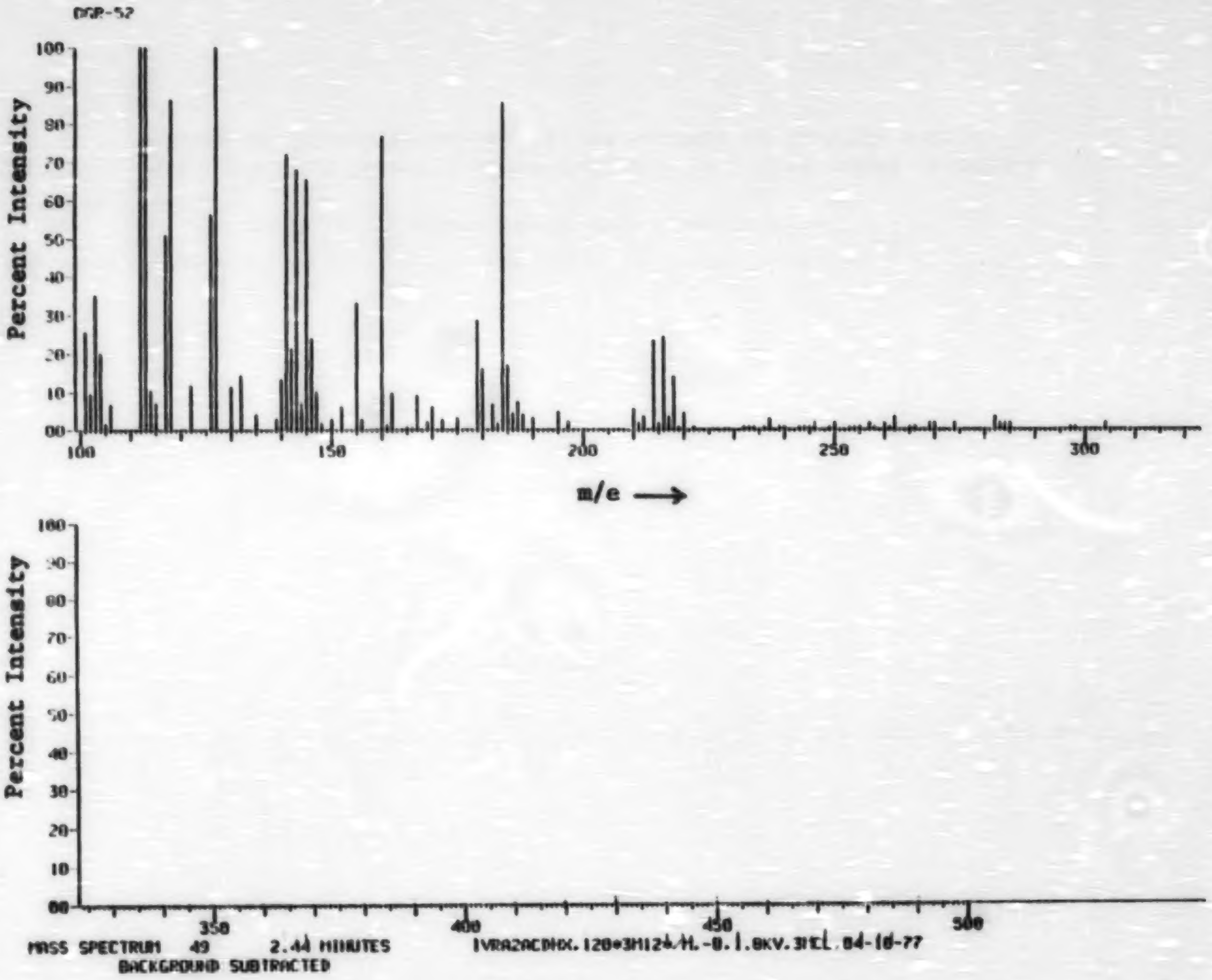

Figure C-63. Mass spectrum of tetrachlorobenzene (M = 214) identified in hexane eluate of diazomethane-methylated extract of Raleigh sludge.

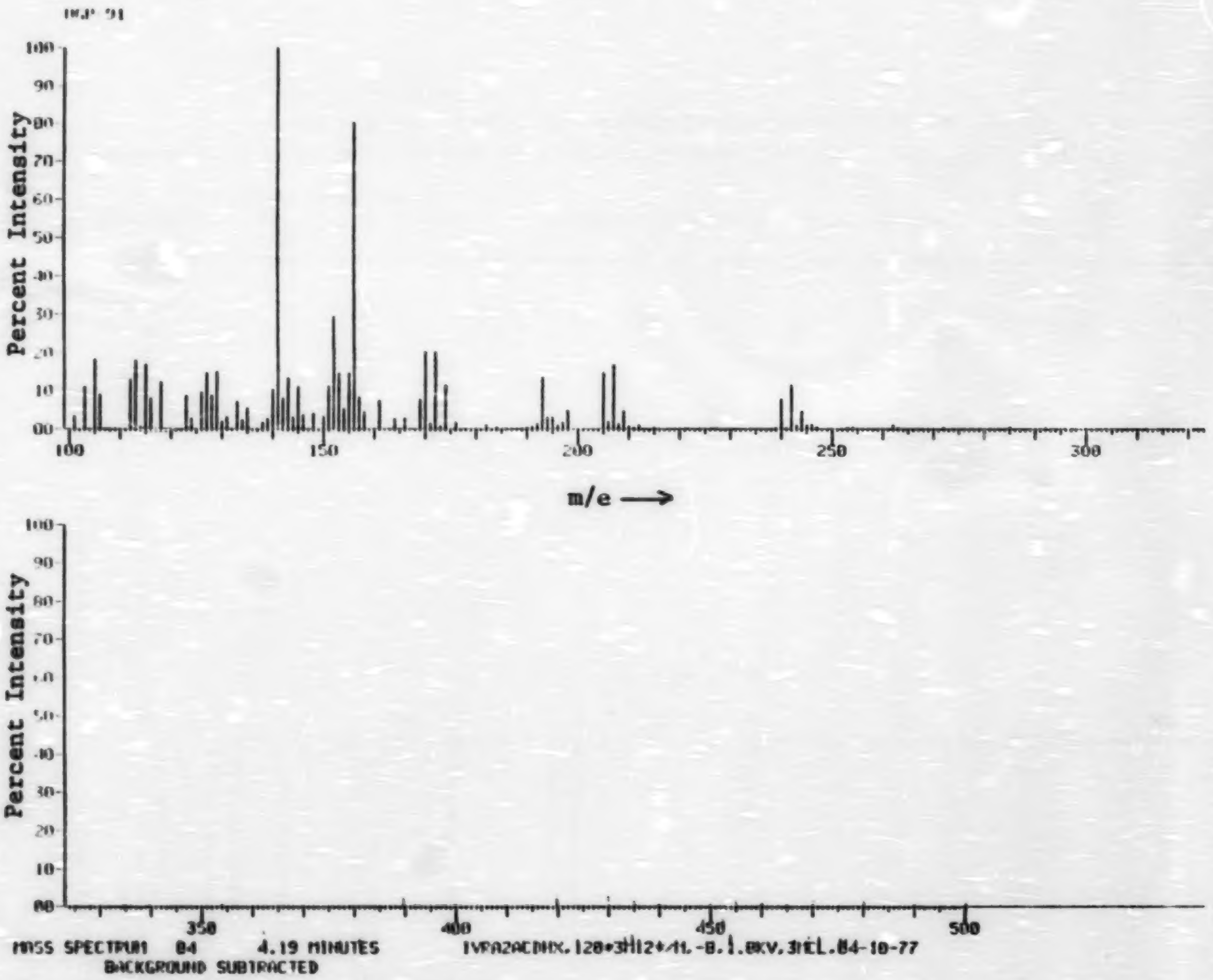

Figure C-64. Mass spectrum of tetrachloro-compound (M = 240) found in hexane eluate of diazomethane-methylated extract of Raleigh sludge.

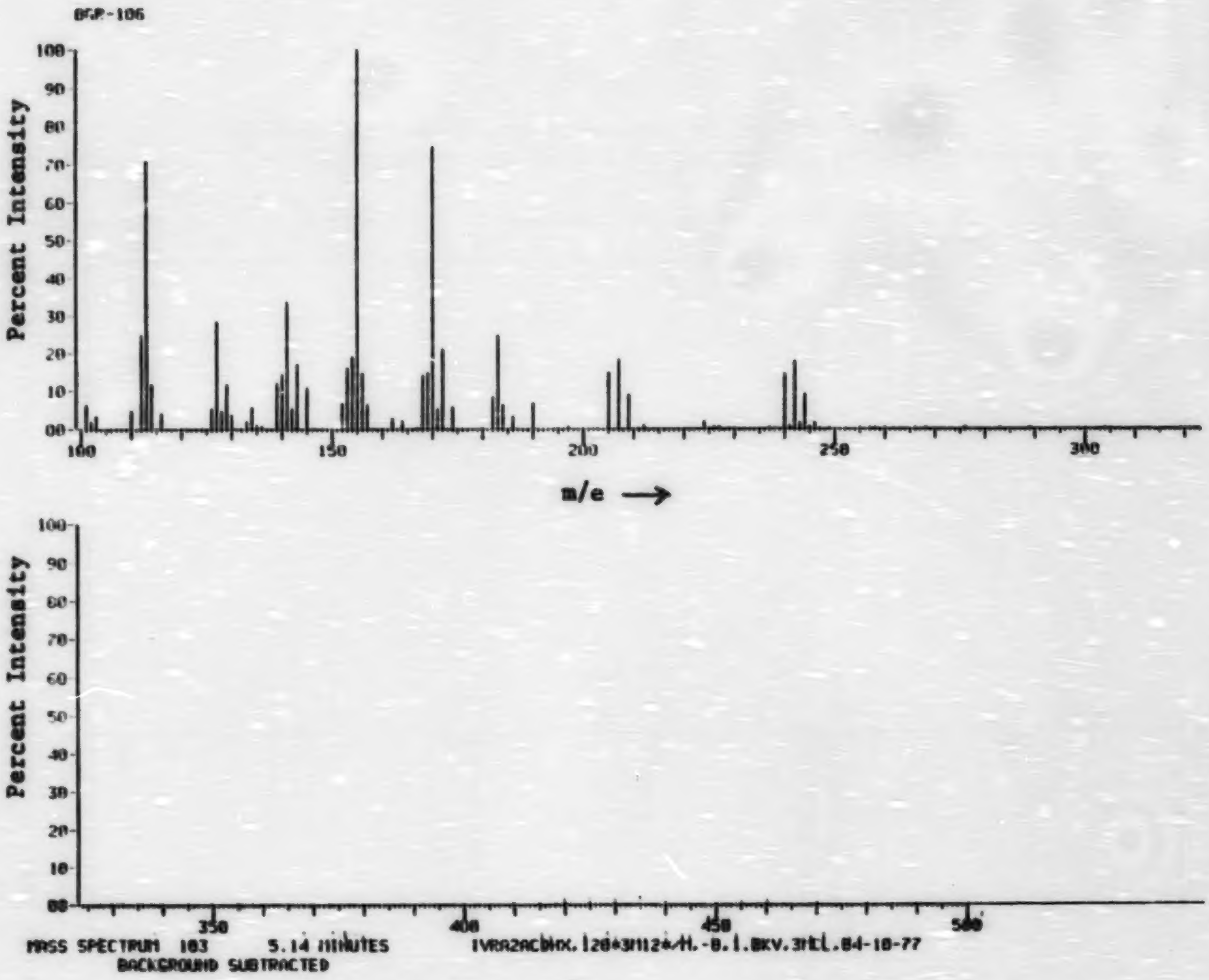

Figure C-65. Mass spectrum of tetrachloro-compound (M = 240) found in hexane eluate of diazomethane-methylated extract of Raleigh sludge.

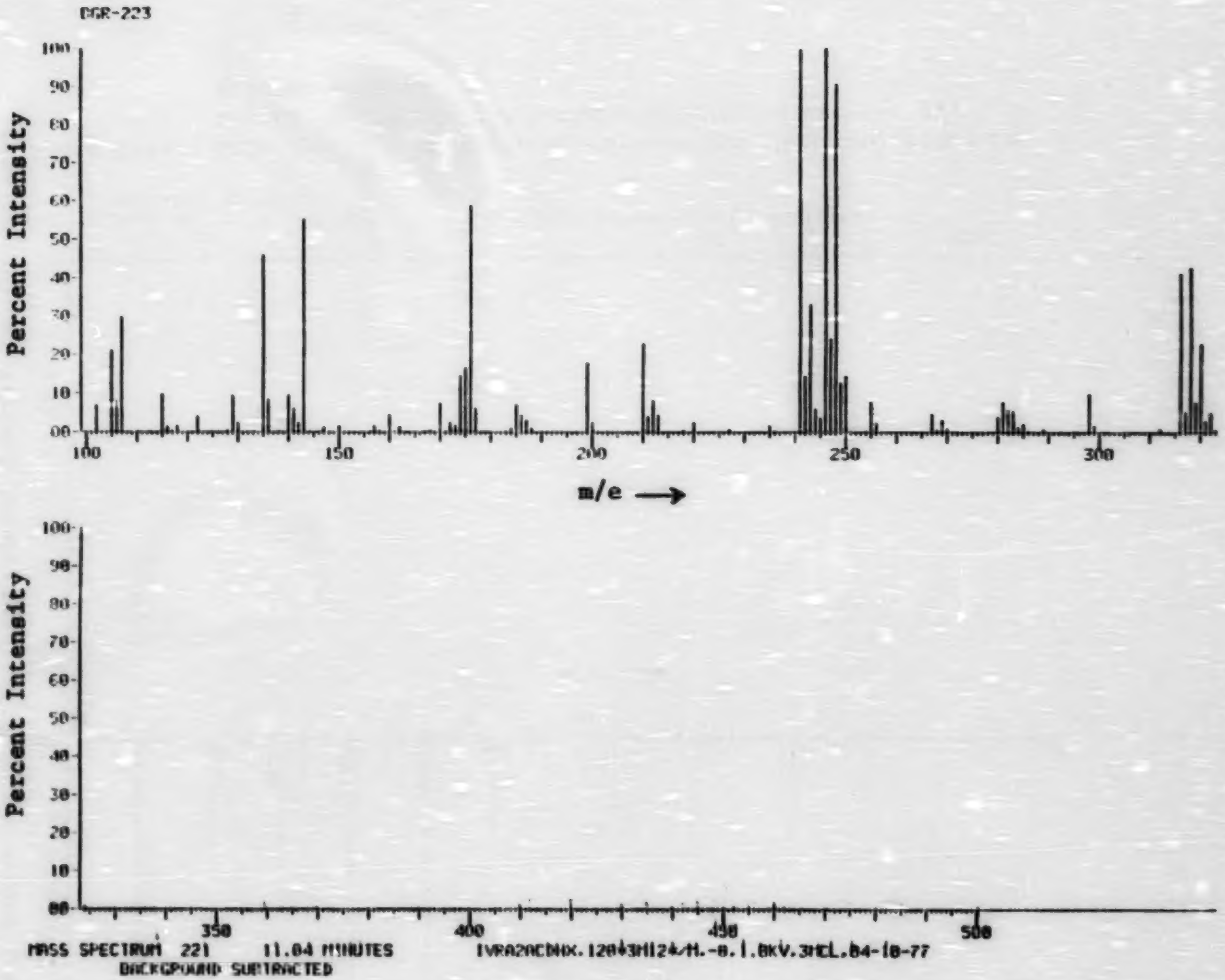

Figure C-66. Mass spectrum of DDE (M = 316) identified in hexane eluate of diazomethane-methylated extract of Raleigh sludge.

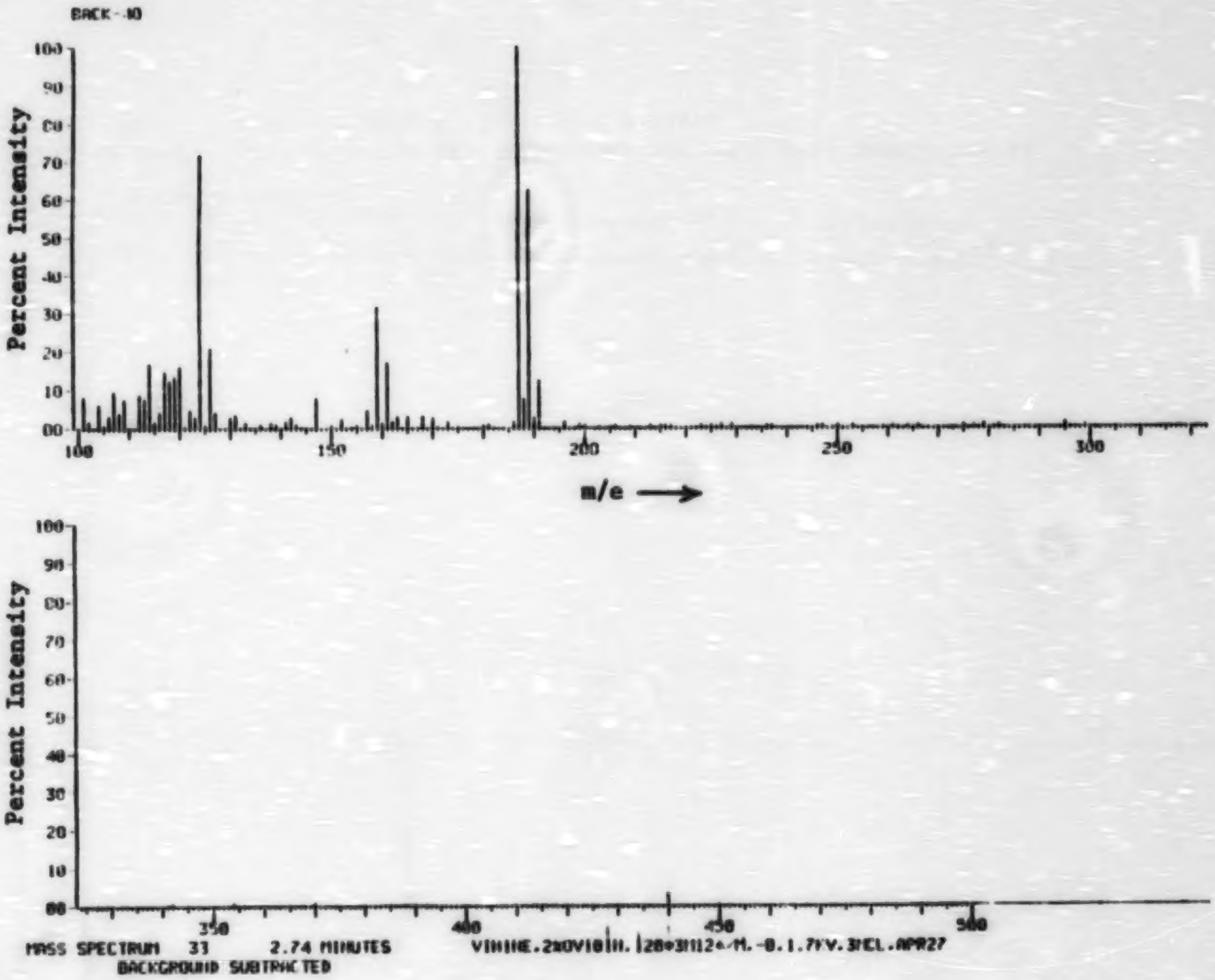

Figure C-67. Mass spectrum of dichloro-compound (M = 187) found in neutral extract of Houston sludge.

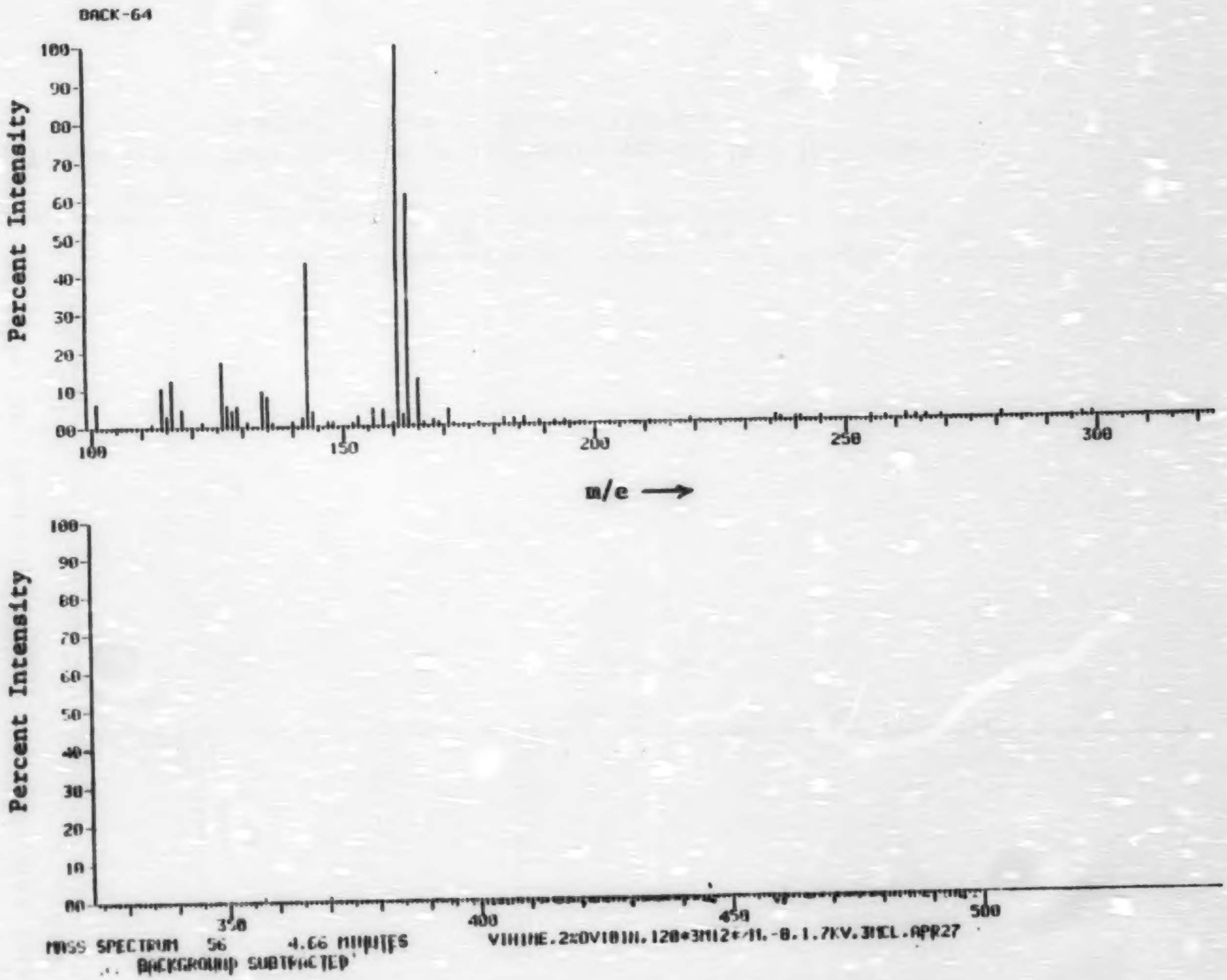

Figure C-68. Mass spectrum of dichloroaniline (M = 161) identified in neutral extract of Houston sludge.

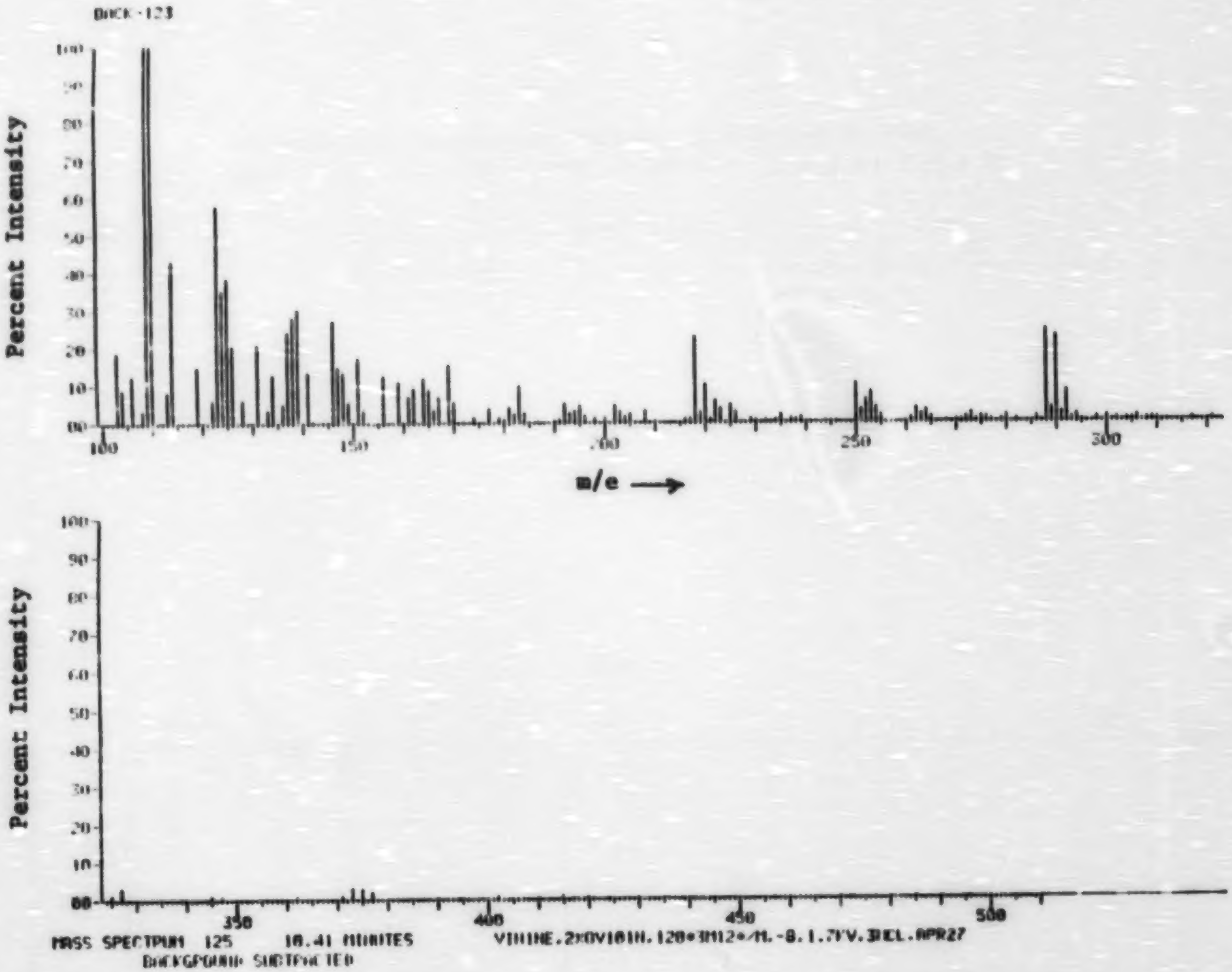

Figure C-69. Mass spectrum of trichloro- compound (M = 288) found in neutral extract of Houston sludge.

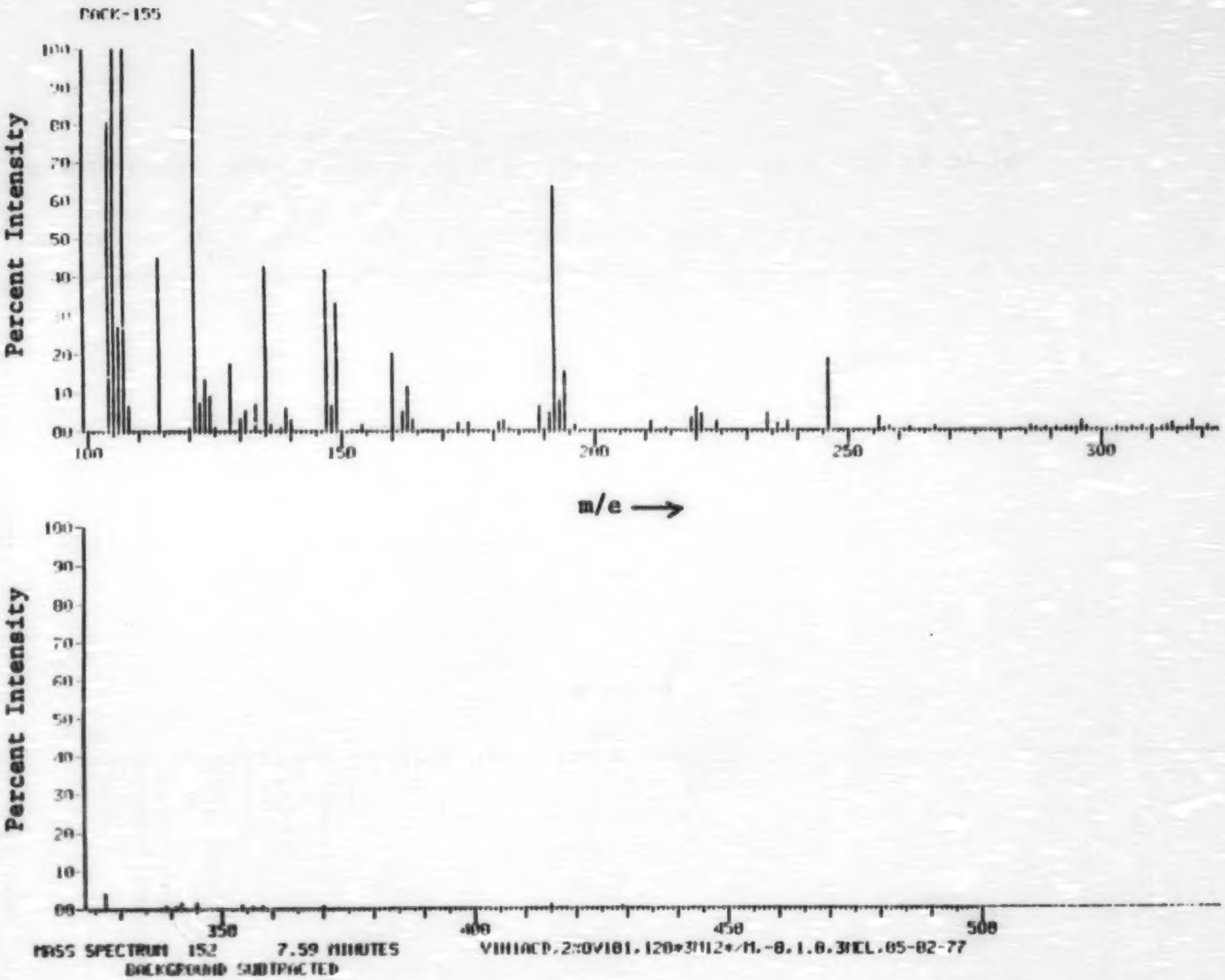

Figure C-70. Mass spectrum of monochloro-compound (M = 192) found in diazomethane-methylated extract of Houston sludge.

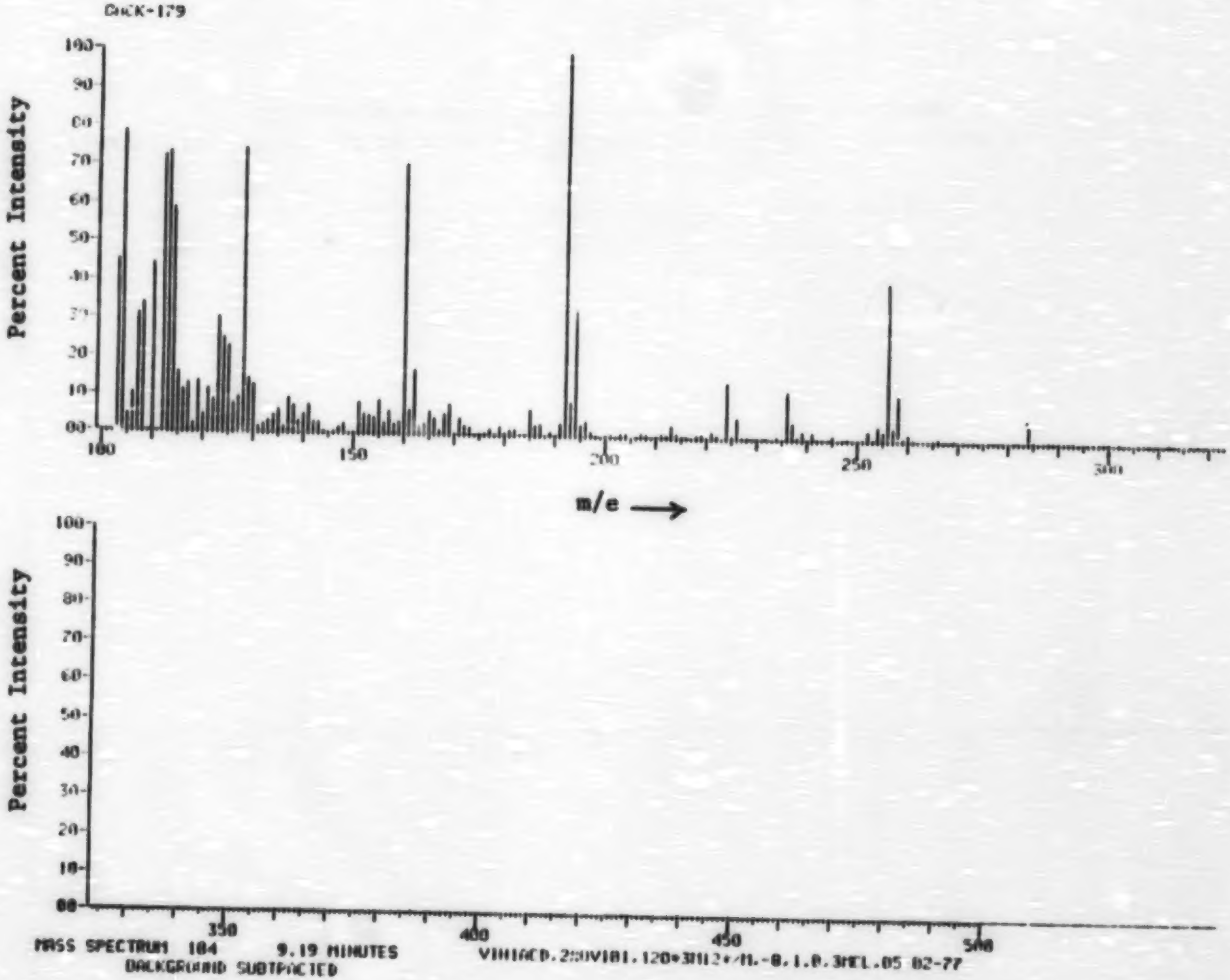

Figure C-71. Mass spectrum of monochloro-compound (M = 256) found in diazomethane-methylated extract of Houston sludge.

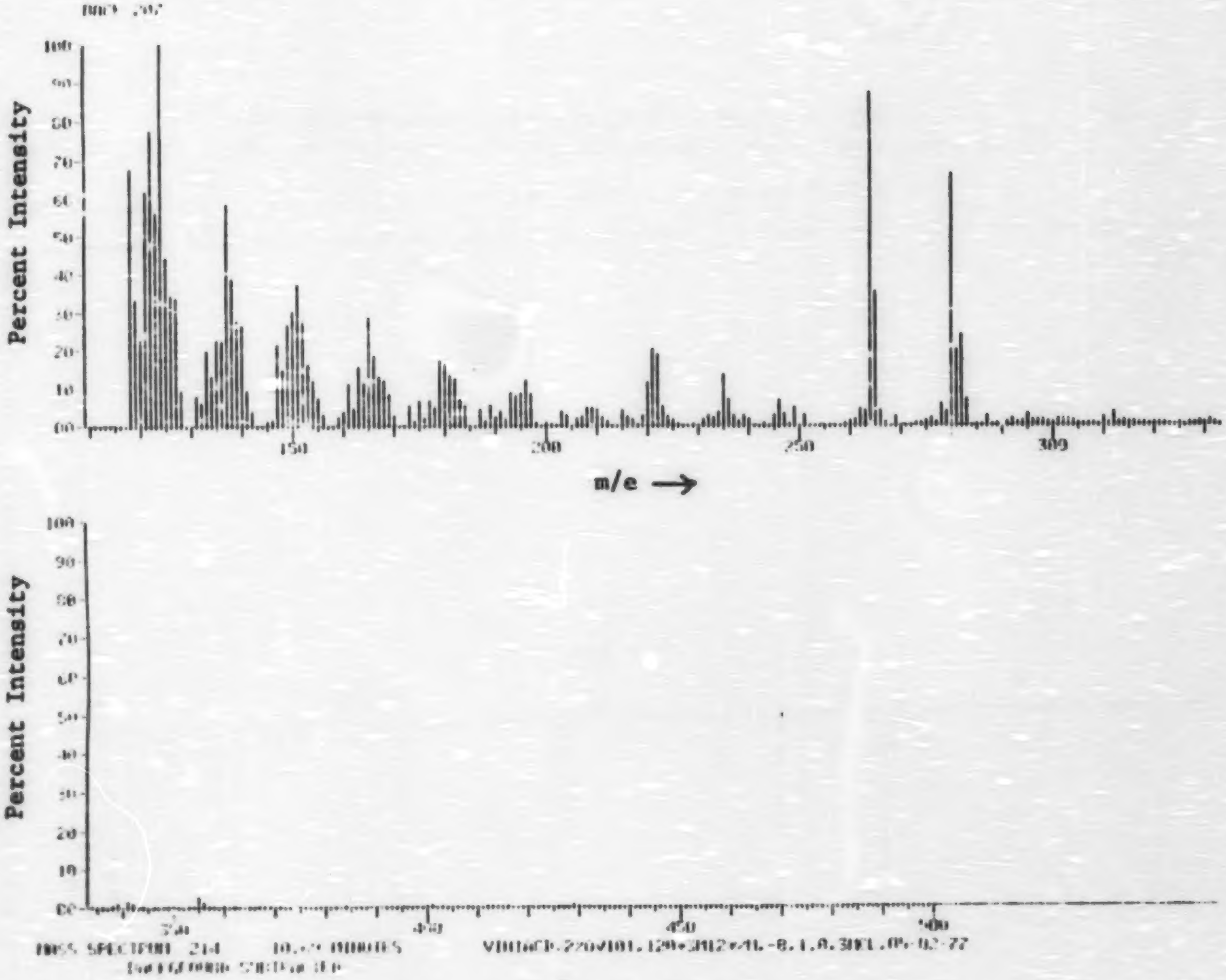

Figure C-72. Mass spectrum of monochloro-compound (M = 280) found in diazomethane-methylated extract of Houston sludge.

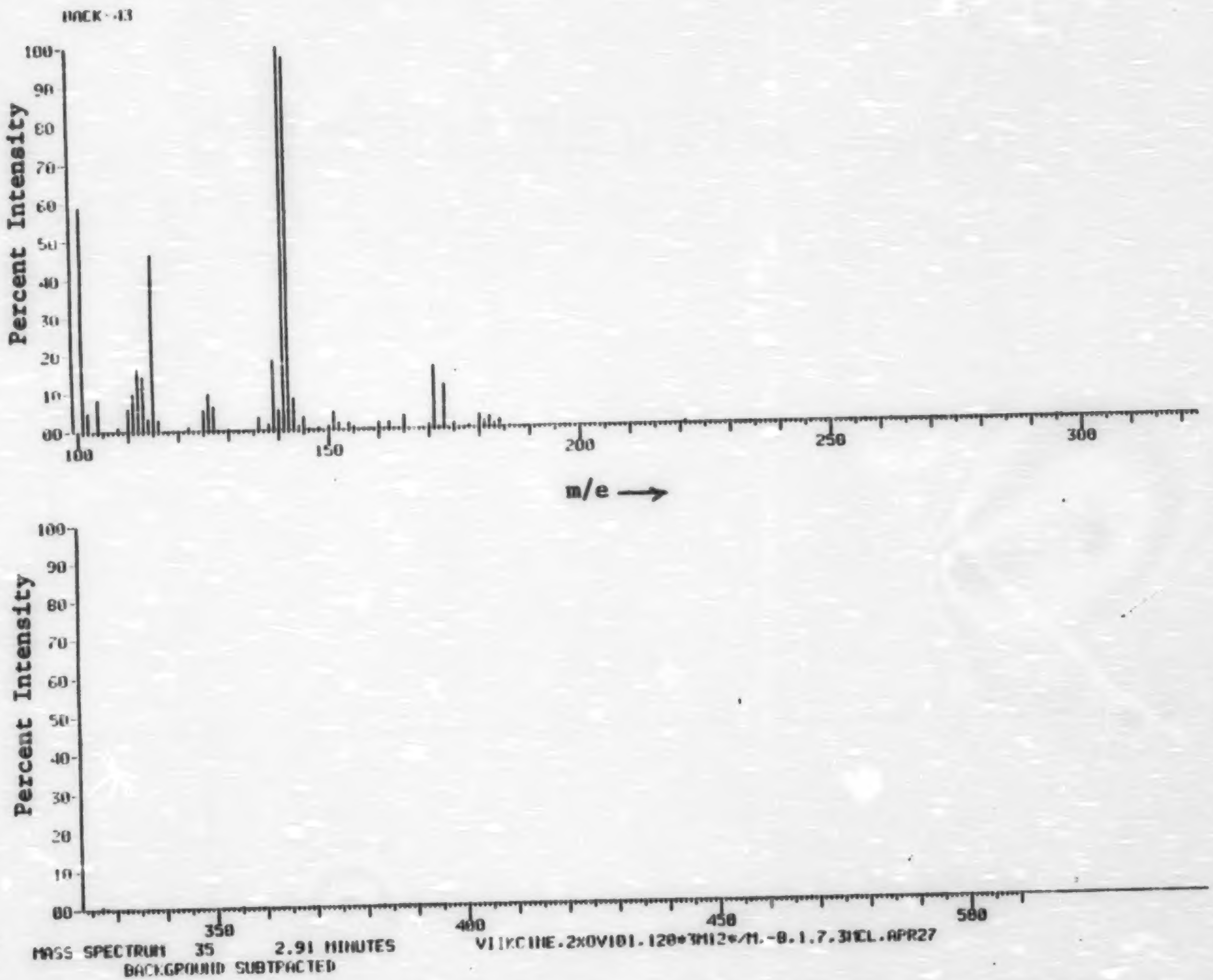

Figure C-73. Mass spectrum of dichloro-compound (M = 171) tentatively found in neutral extract of Kansas City sludge.

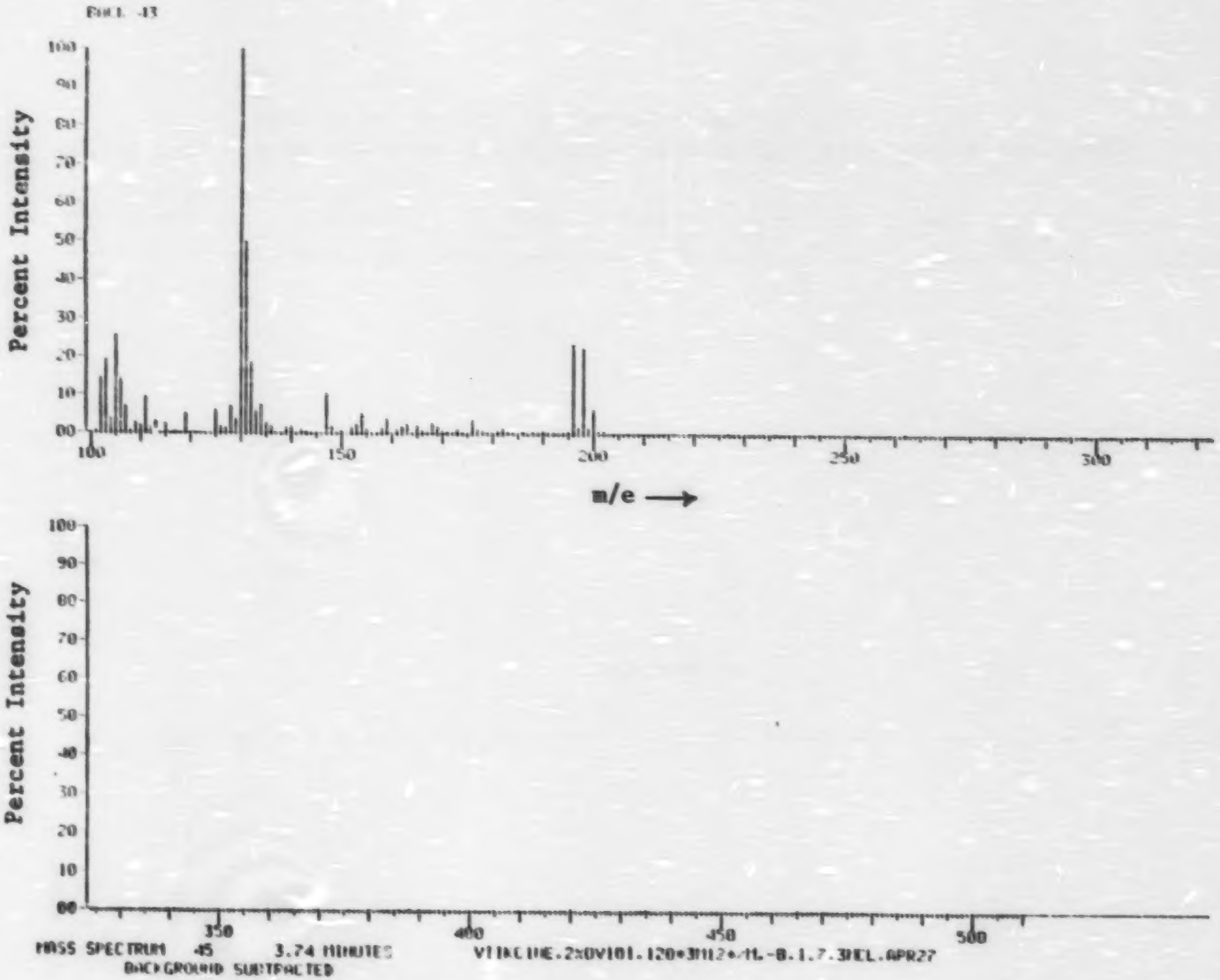

Figure C-74. Mass spectrum of trichlorophenol (M = 196) identified in neutral extract of Kansas City sludge.

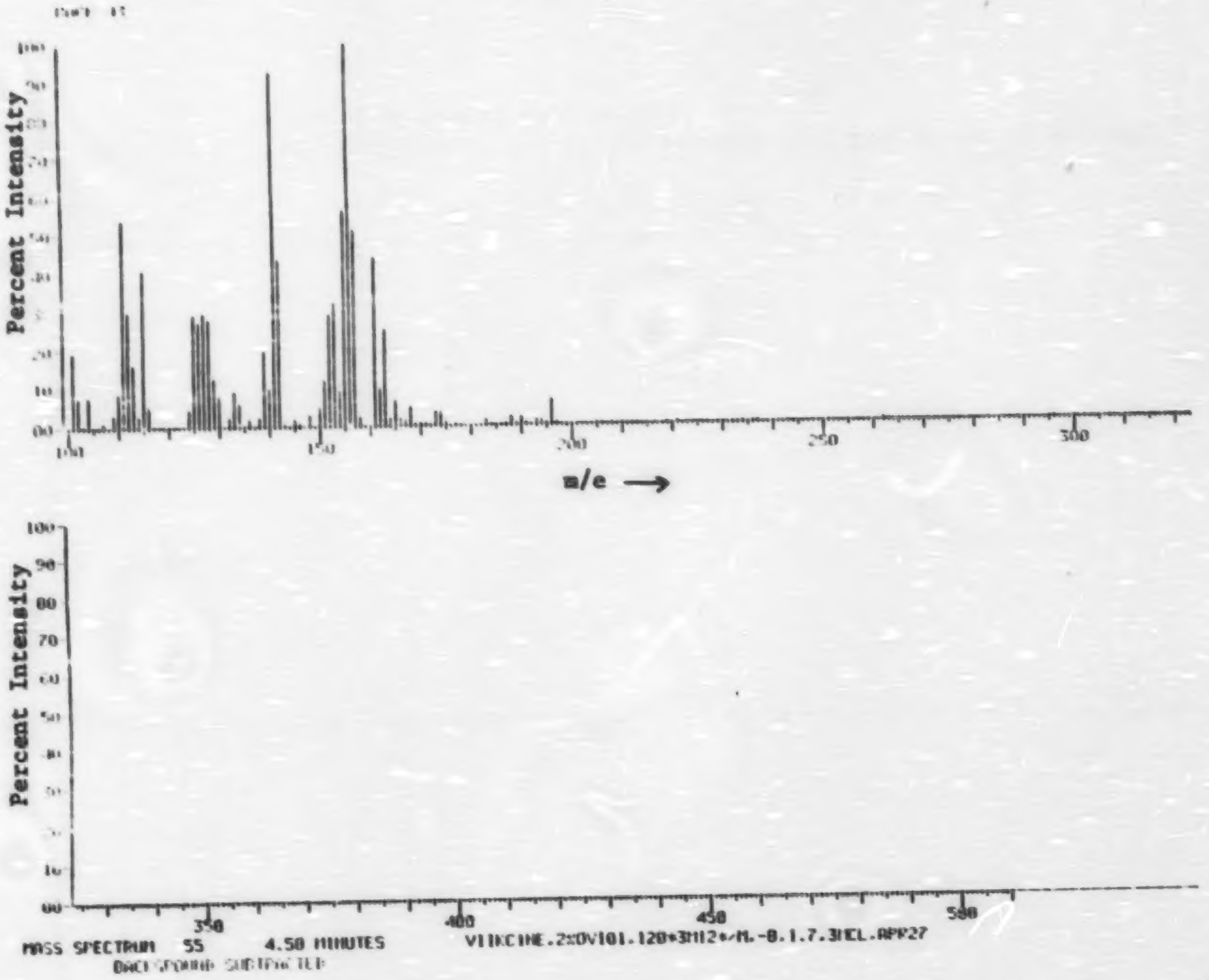

Figure C-75. Mass spectrum of dichloroaniline (M = 161) tentatively identified in neutral extract of Kansas City sludge.

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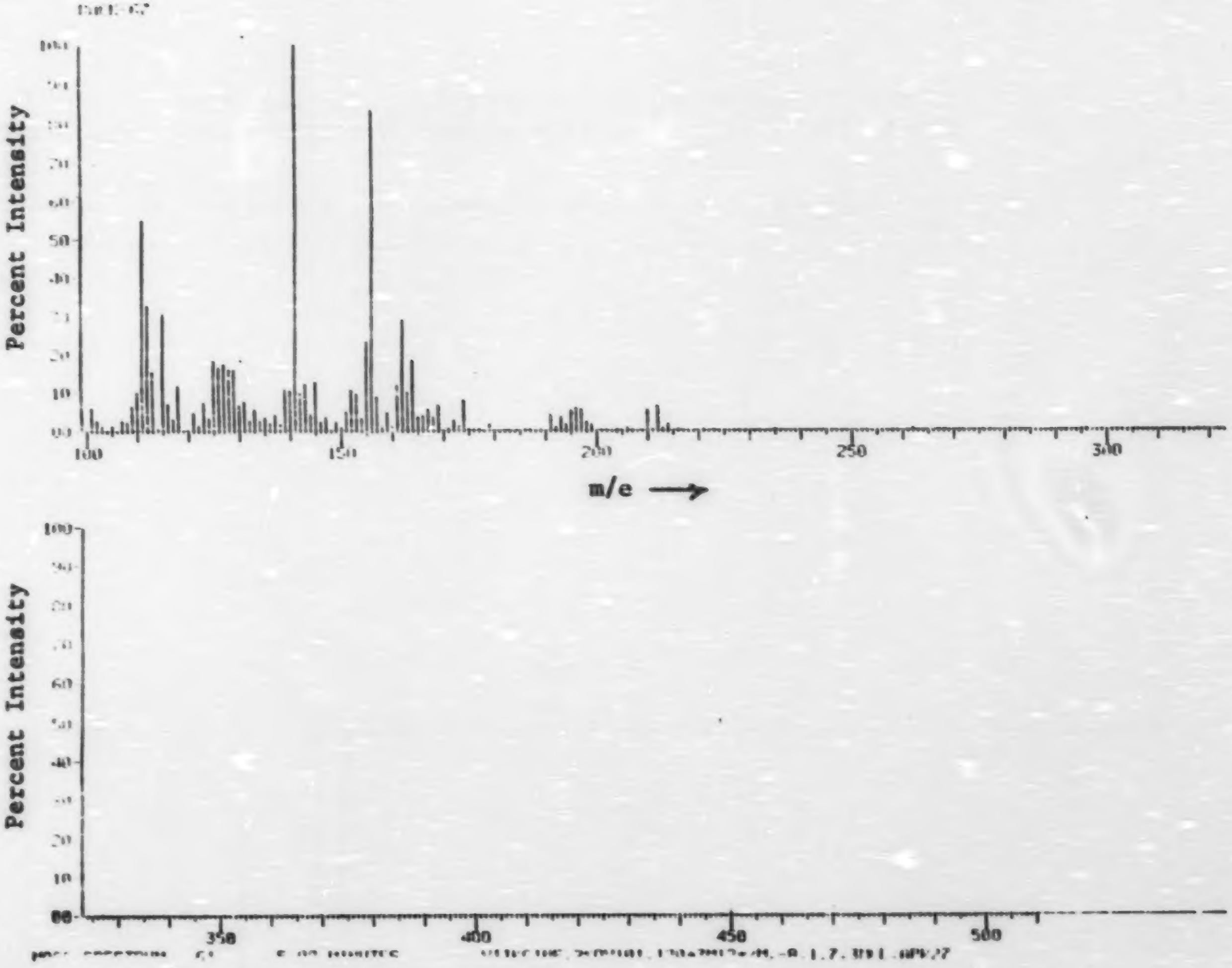

Figure C-76. Mass spectrum of trichloro-compound (M = 210) found in neutral extract of Kansas City sludge.

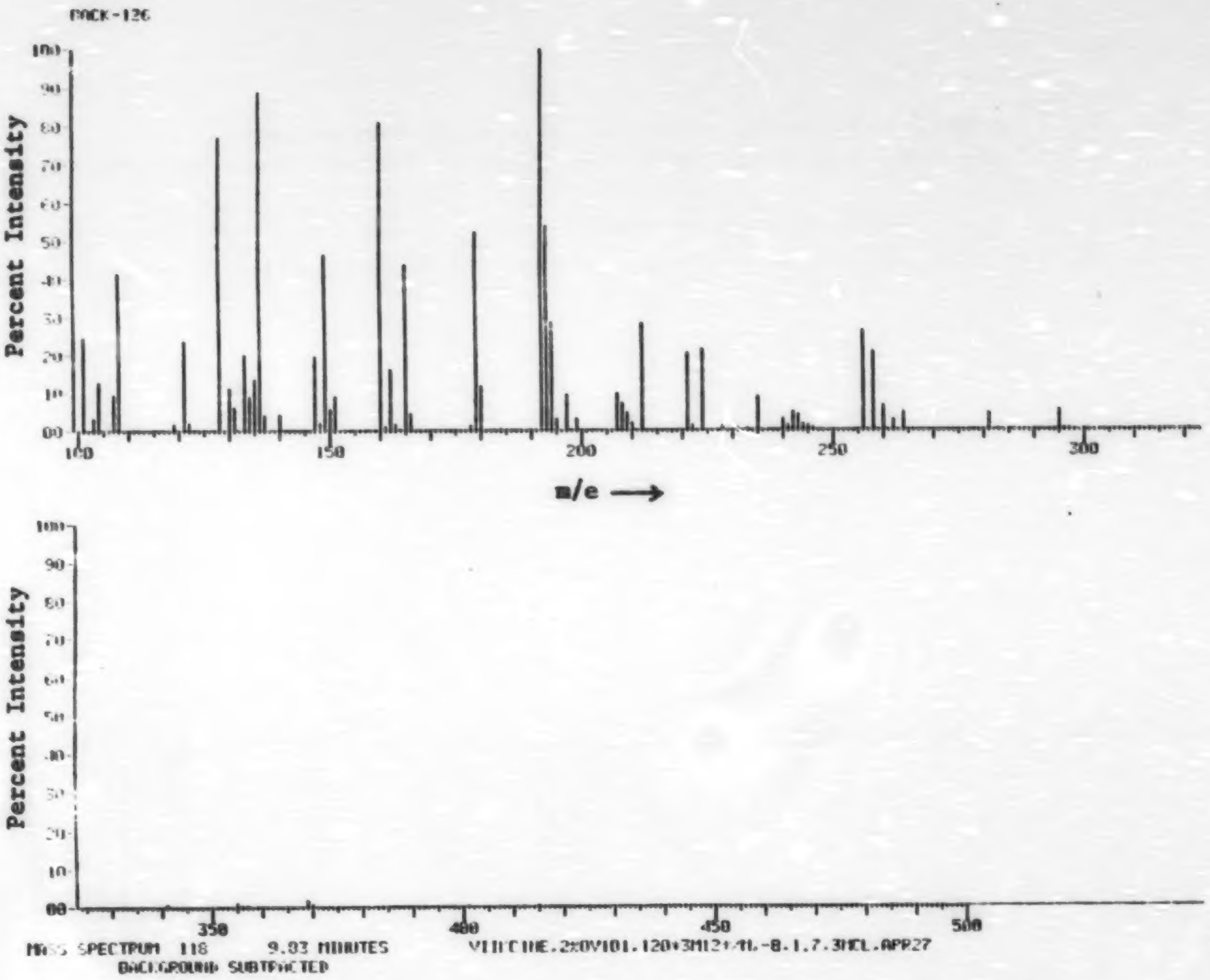

Figure C-77. Mass spectrum of trichlorobiphenyl (M = 256) identified in neutral extract of Kansas City sludge.

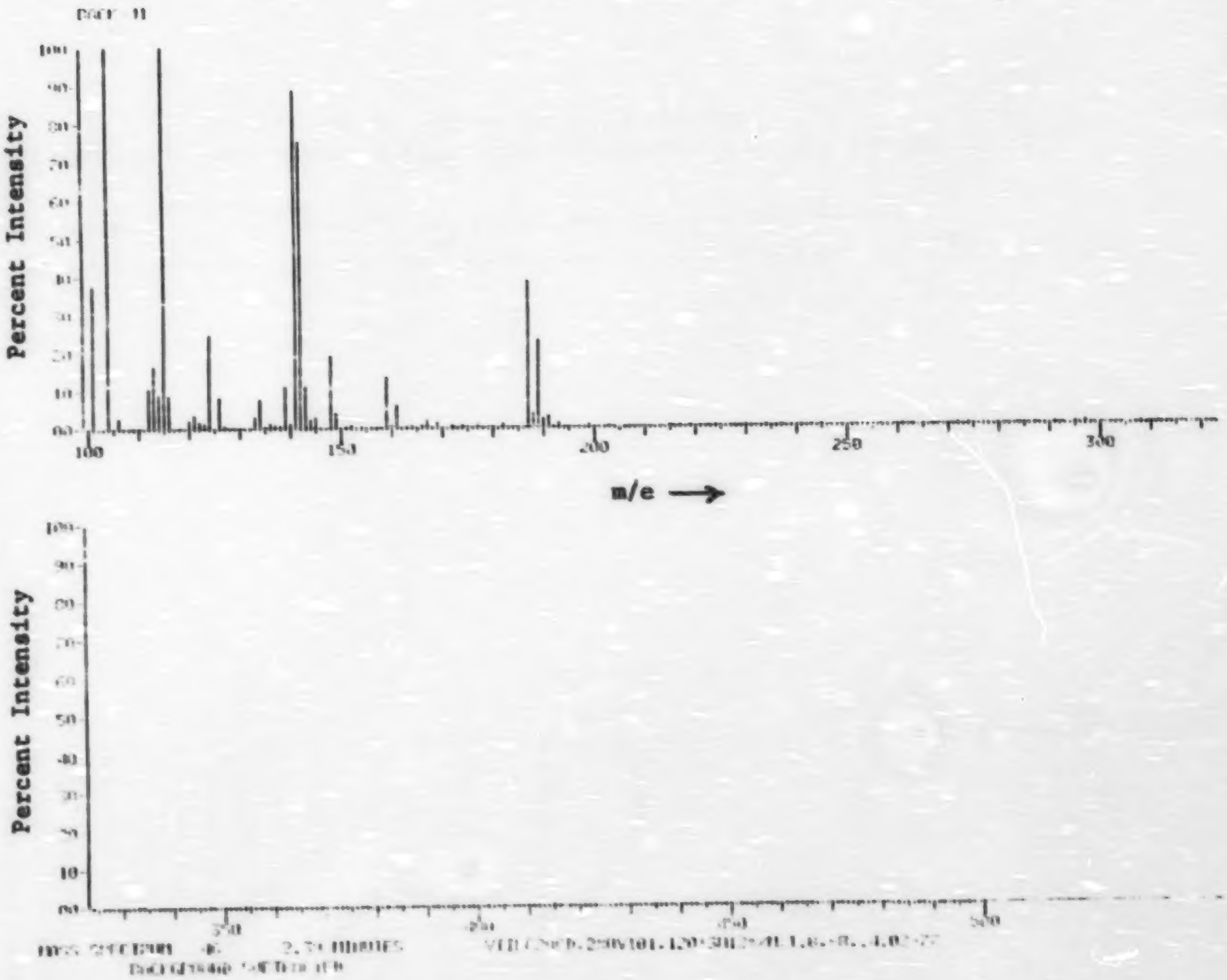

Figure C-78. Mass spectrum of dichloro-compound (M = 187) found in diazomethane-methylated extract of Kansas City sludge.

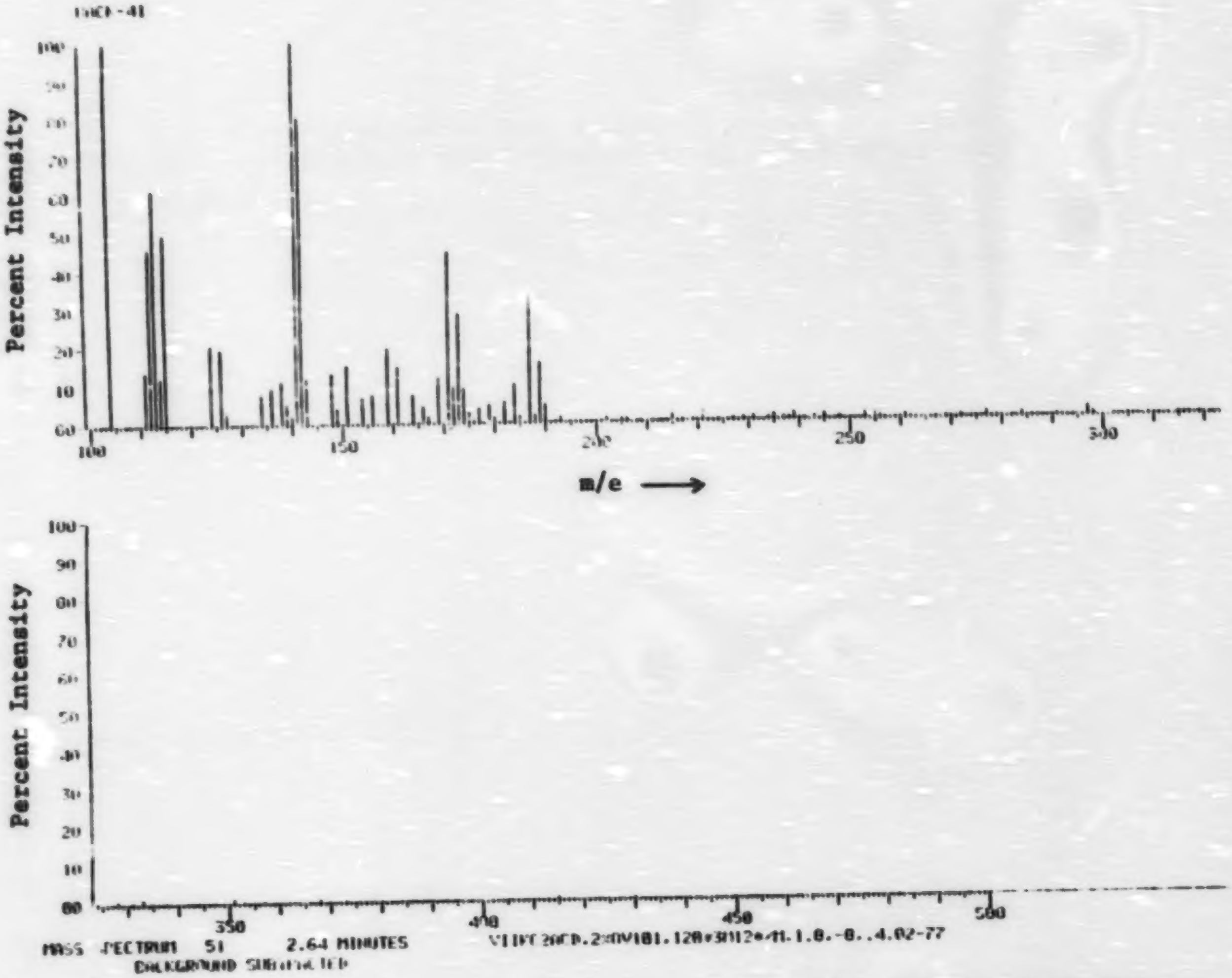

Figure C-79. Mass spectrum of dichloro-compound (M = 171) found in diazomethane-methylated extract of Kansas City sludge. [Note: Cl cluster at m/e = 197 is from a different compound -- see previous spectrum].

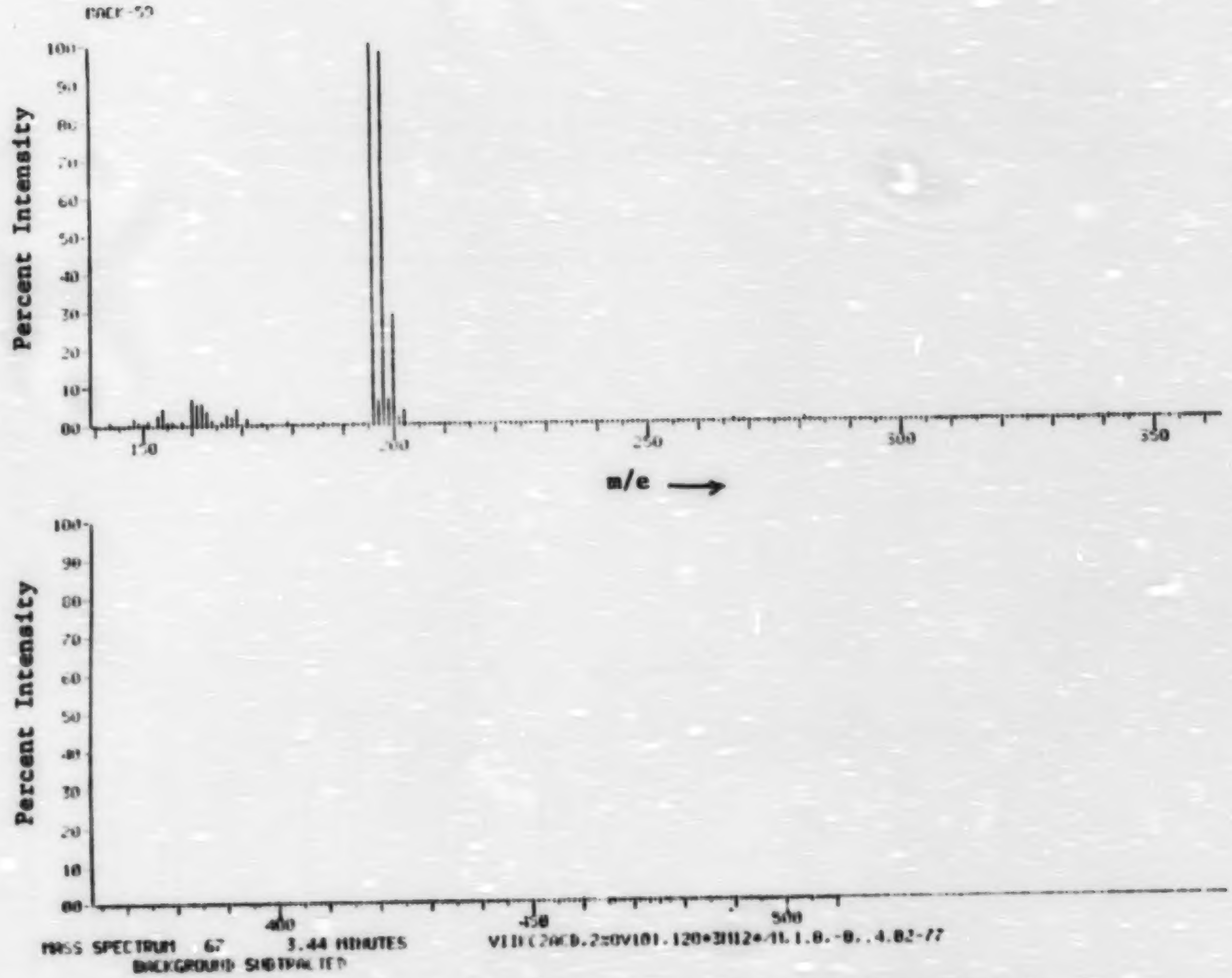

Figure C-80. Mass spectrum of trichlorophenol (M = 196) identified in diazomethane-methylated extract of Kansas City sludge.

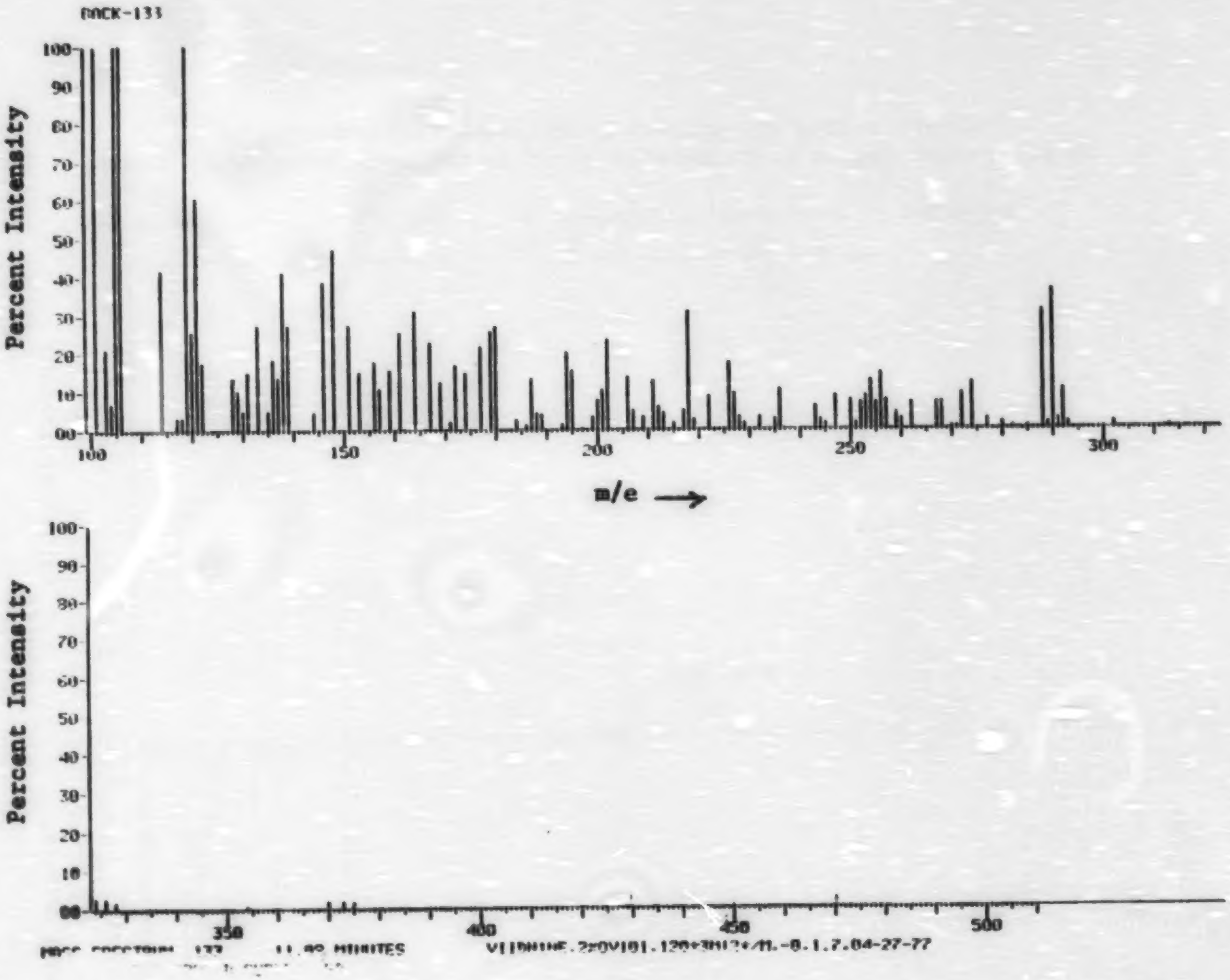

Figure C-81. Mass spectrum of trichloro-compound (M = 288) found in neutral extract of Denver sludge.

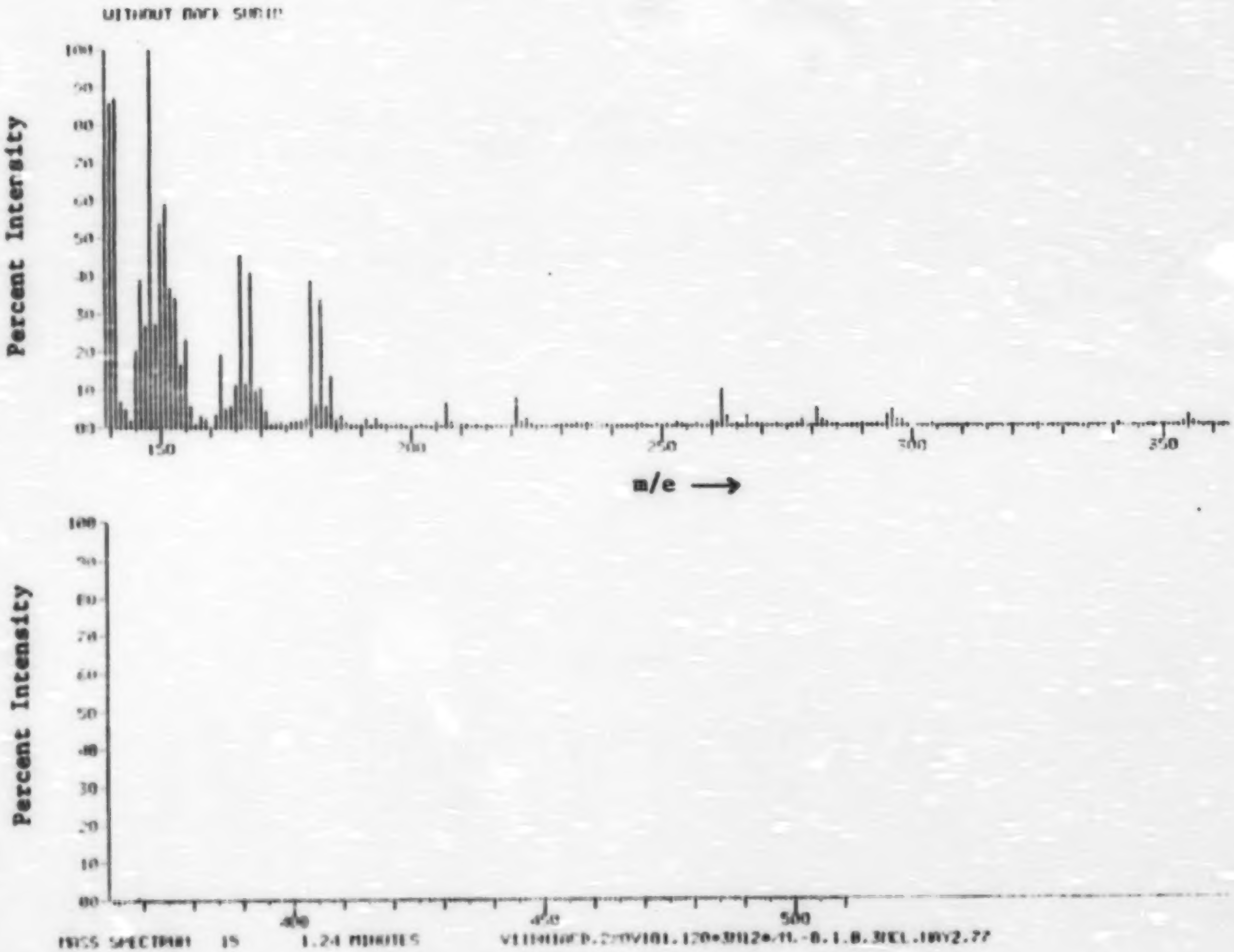

Figure C-82. Mass spectrum of trichlorobenzene (M = 180) identified in diazomethane-methylated fraction of Denver sludge.

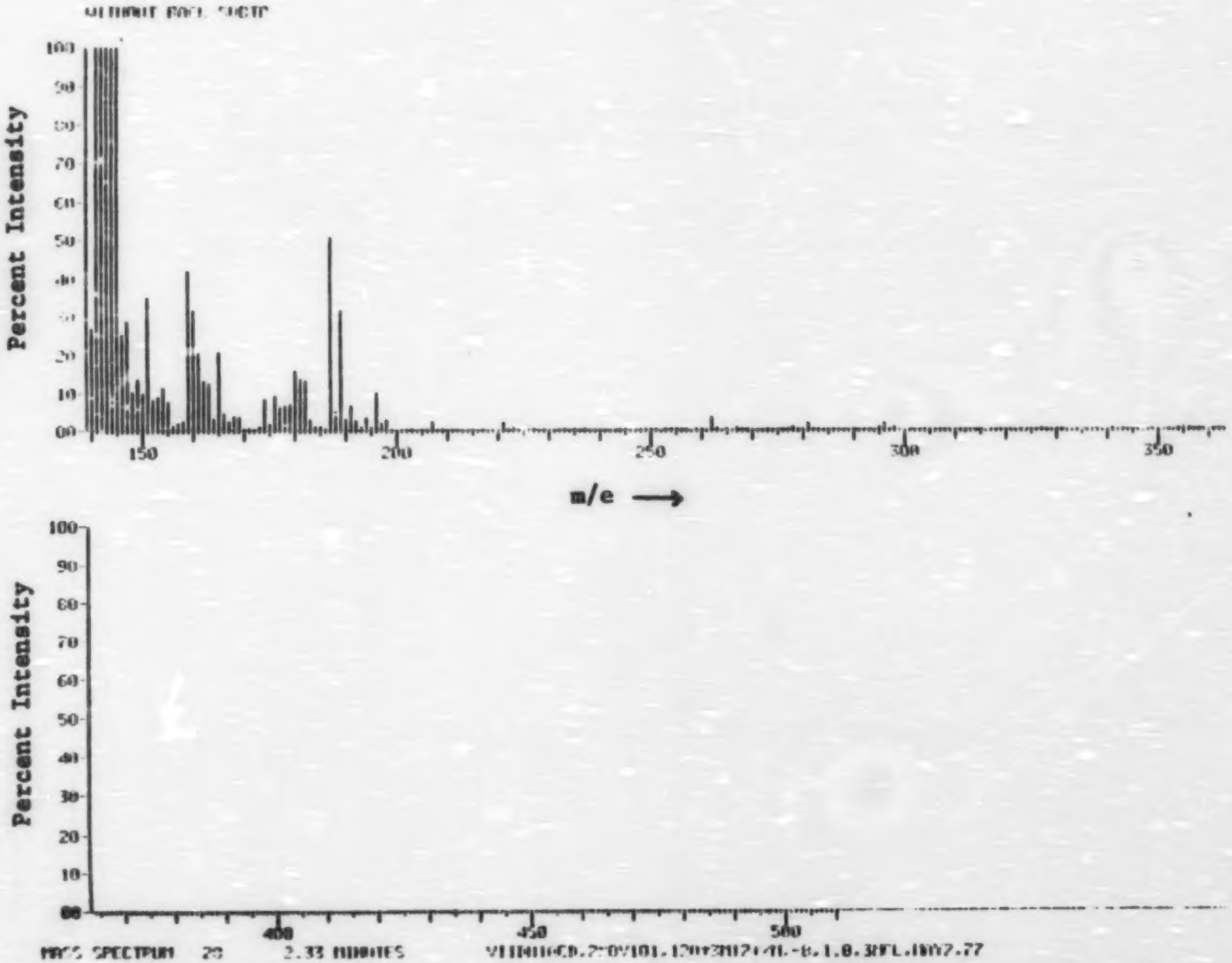

Figure C-83. Mass spectrum of dichloro-compound (M = 187) found in diazomethane-methylated extract of Denver sludge.

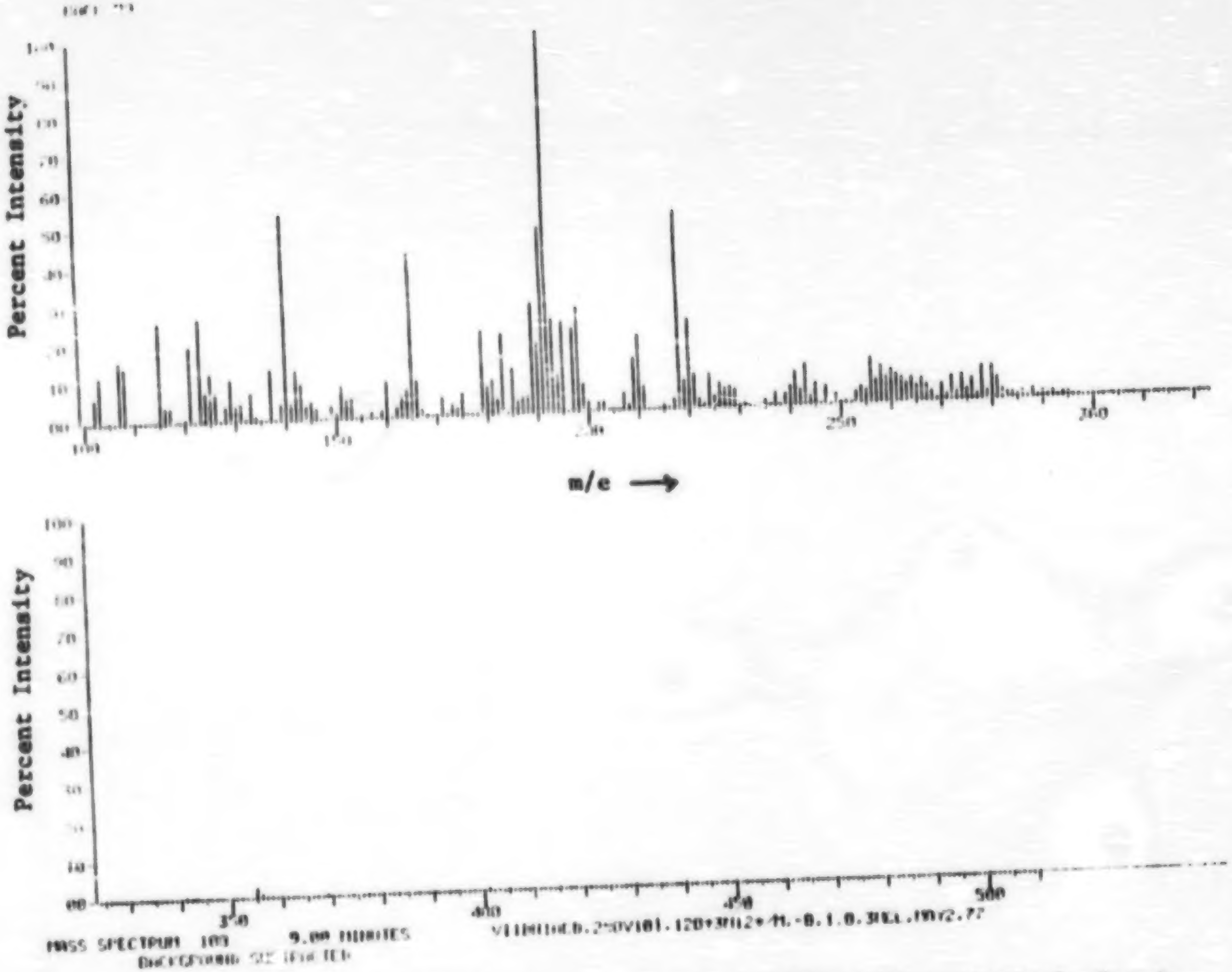

Figure C-84. Mass spectrum of monochloro-compound (M = 218) tentatively found in diazomethane-methylated extract of Denver sludge.

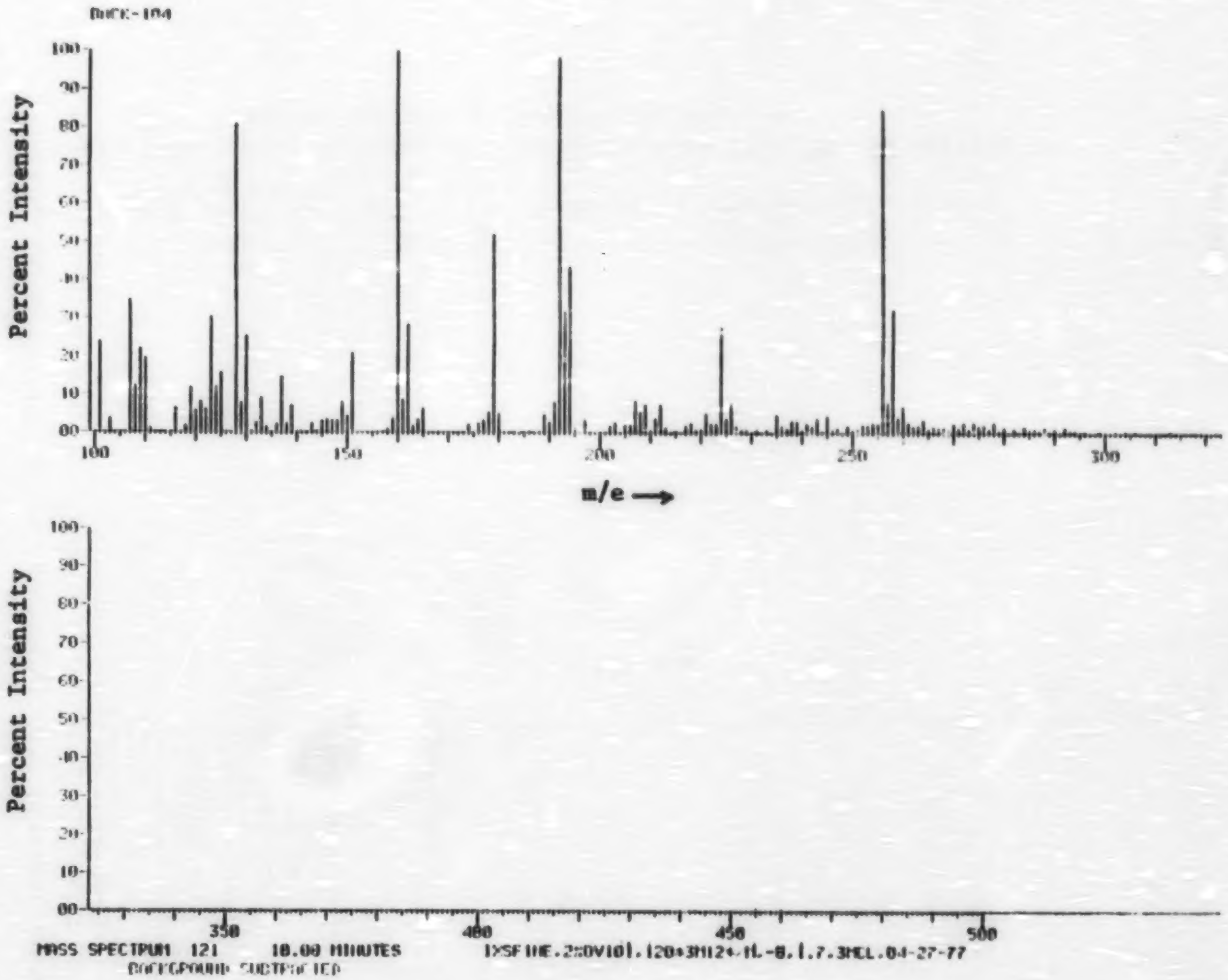

Figure C-85. Mass spectrum of dichloro-compound (M = 256) found in neutral extract of San Francisco sludge.

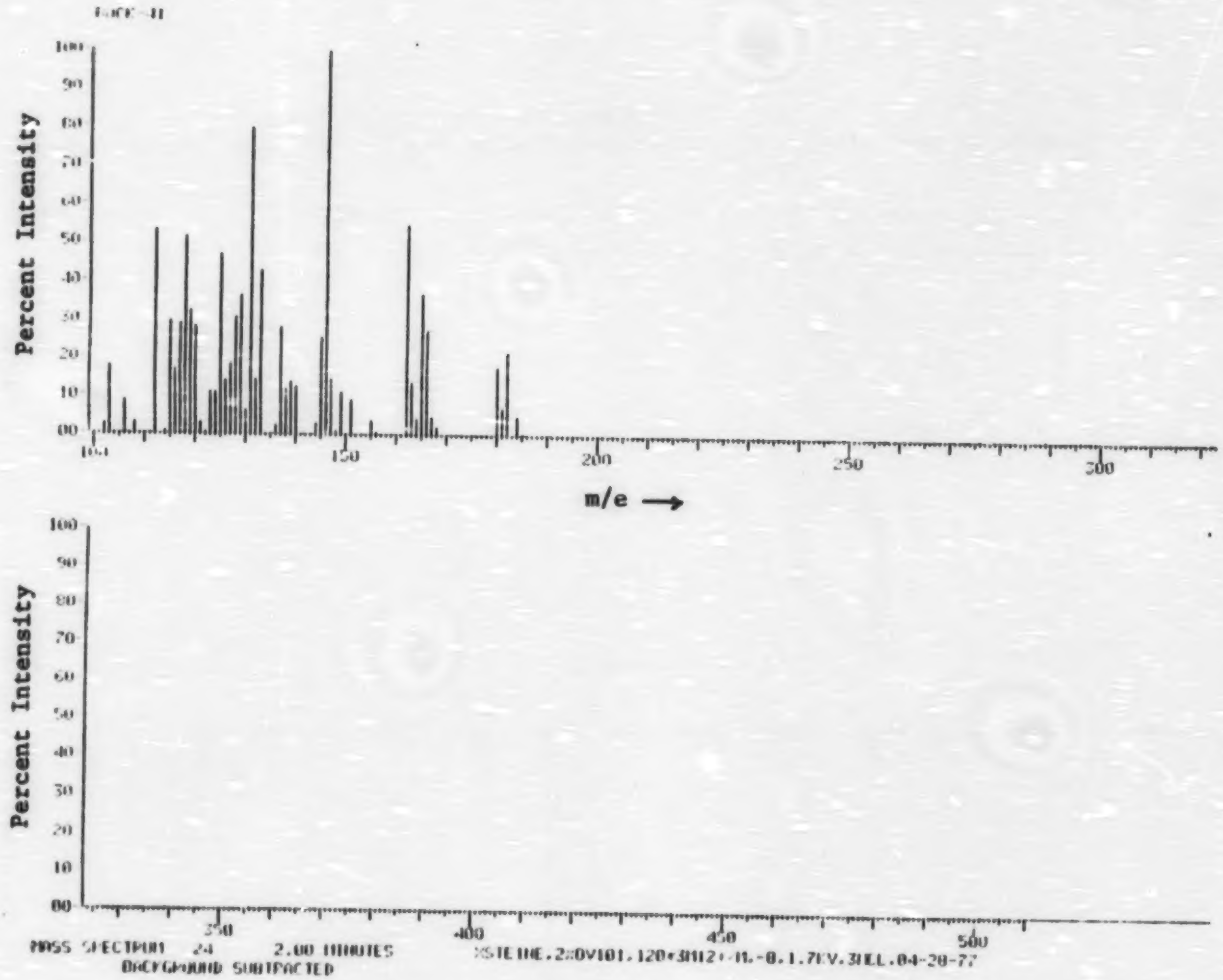

Figure C-86. Mass spectrum of trichlorobenzene (M = 180) identified in neutral extract of Seattle sludge.

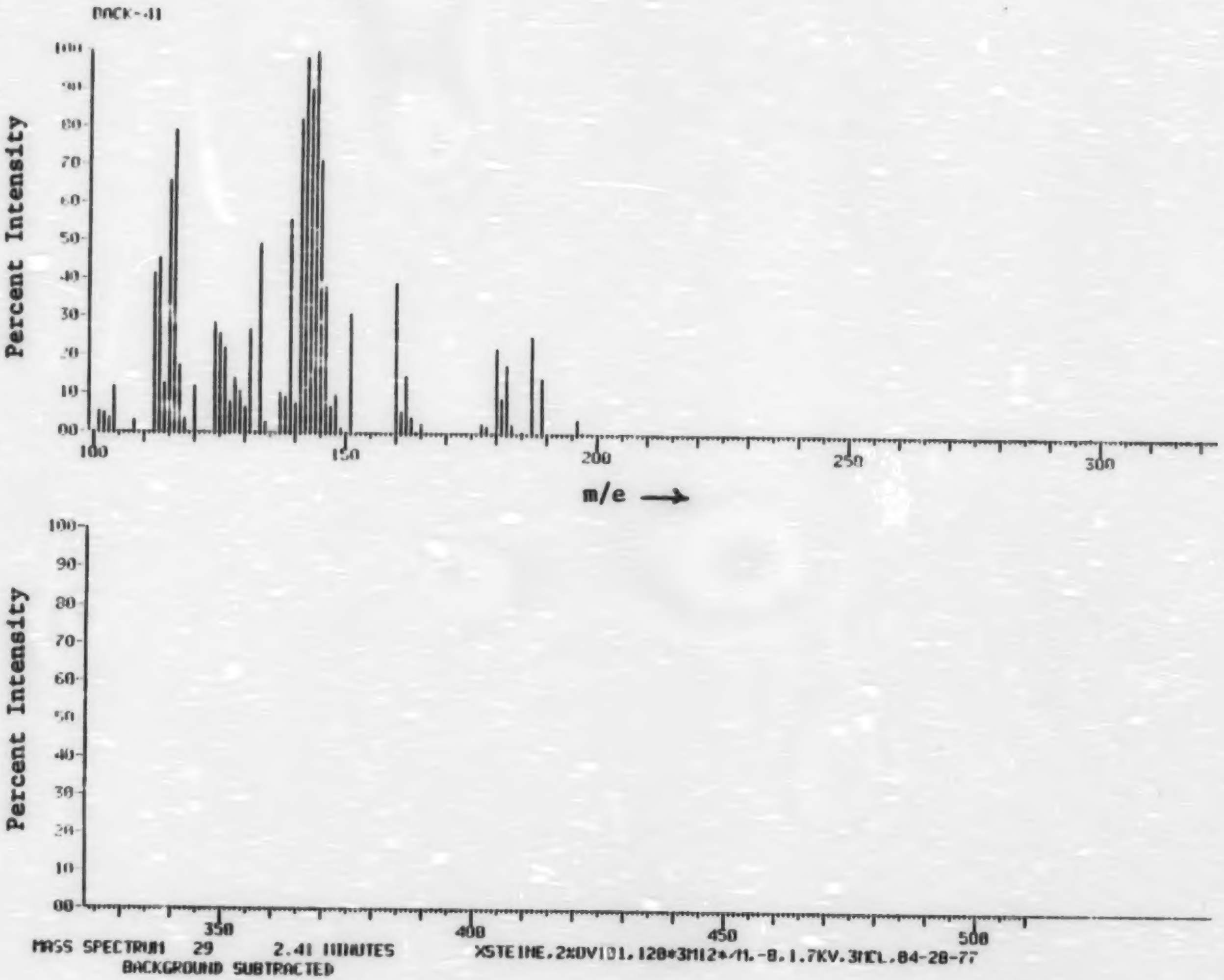

Figure C-87. Mass spectrum of dichloro-compound (M = 187) found in neutral extract of Seattle sludge.